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THE NITROGEN INDUSTRY

THE
NITROGEN INDUSTRY

BY

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PREFACE

TWENTY years ago the Nitrogen Industry attracted very little general attention. The supplies of combined nitrogen requisite for the needs of agriculture and the useful arts, including the manufacture of explosives, were apparently assured by the nitrate deposits of Chile and the sulphate of ammonia obtained as a by-product in the coking and gas-making industries. Since that time, however, the so-called Nitrogen Problem has become increasingly important. The two sources of supply mentioned have been extended, the first by the introduction of slightly improved methods of extraction, and the second by an increasing use of plant for the recovery of ammonia, formerly wasted in large quantities by carrying out the coking process in a crude and inefficient manner. It has become increasingly clearer that these two sources of fixed nitrogen are alone insufficient to supply the growing needs of mankind, and attention has therefore been more and more focussed on the master problem of obtaining from the boundless stores of uncombined nitrogen in the atmosphere, by economical methods, those nitrogen compounds, principally ammonia and nitric acid, which are required in the raising of food crops, and in the prosecution of war. Mars and Ceres both imperatively demand combined nitrogen, and the homage paid to both by man has sharpened his ingenuity to a degree which might have been impossible under the reign of less attractive deities. The Great War of 1914-18 called for nitrogen compounds in the form of explosives on a scale hitherto unprecedented. The enemy, cut off from the Chilean supplies, was able rapidly to put into large-scale operation the new methods for the fixation of atmospheric nitrogen which he had perfected by laborious and costly experimental research but a few years prior to the outbreak of hostilities. Without this assistance the defeat of the Central Powers would have been speedy and complete. The Allies, maintaining at immense cost the real supremacy of sea-power, had open to them at first only the old source of Chile, and for a long time relied on this to a dangerously exclusive degree. In 1918 the extension of the submarine blockade instituted by Germany led to a state of affairs which at one time was perilous in the extreme. Ships carrying nitrate from Chile were sunk, but, what was far more important, ships which should have brought food were diverted to the transport of nitrate, and, in the later stages of the War, of finished explosives. France was the first allied power to take adequate steps to meet the peril, and at the time of the Armistice was well on the way to becoming self-supporting in fixed nitrogen for explosives. America, on her timely entry into the struggle, made preparations on a most imposing scale for the manufacture of nitrogen compounds from the air. Italy had made more modest, but none the less solid, contributions to the solution of the problem. Great Britain alone was the one allied country which failed most signally to do her share of the work, as she is now the only great power in the world which has not within the gates of her territory the necessary means for the synthetic production of nitrogen compounds for the purposes of peace and war. Amidst the noise and clamour which have raged around the initiation and protection of the so-called "Key Industries," no voice has been heard on the greatest, the most important key industry of all. Without explosives and food, the home production of a few fine chemicals and a few tons of glass used in chemical laboratories will be but sorry comfort in the next war, on the assumption of which the supporters of "key industries" largely rely for their justification. Why should this state of affairs exist? What steps should be taken to provide a remedy? Why, after the bitter experience of war, should we still remain helplessly dependent on a foreign power for our food and explosives? These are matters which, we think, should appeal to a large public. We believe we are right in asserting that, since the War, there has been a growing demand on the part of the public for real information. The ordinary man has learned to distrust information doled out from on high in a specially prepared form.

He was not unmindful of "propaganda" during the War, and has acquired a distaste for it. A large part of the propaganda now appearing in the Press, having for its object the justification of the protection of the dye industry, is based on the assumption that dye factories can, on the possible outbreak of war, be converted into factories for the production of explosives and poison gas. There is a large measure of truth in this. The plant used in the manufacture of intermediates and dyes could be adapted to the manufacture of explosives and gas, although if absolute security were desired the retention of the Government factories would have been more certain, if less economical. One absolutely vital factor has, however, been wholly left out of account, and its neglect completely nullifies the whole argument. Without the necessary materials no factory can be of the slightest service. If nitrates are to be imported from Chile there can be no security, and if the supply were cut off the factories would be idle and impotent. There is no true comparison with the German dye factories. These had at their command internal sources of nitrates, and without them would not have been of the slightest importance. If materials have to be imported to the British factories, why should we not import rather finished explosives? These would make far less demand on shipping. If the dye industry is to succeed it must stand on its own legs. If the British manufacturer can produce better and cheaper wares than his competitors—and there is no reason why he should not—he is assured of success. If he cannot, he ought not to make partial and inaccurate statements which tend to lead those not in possession of the facts to believe that he is the guardian of national security.

From what has been said it should be clear that a nitrogen policy is of importance to the state, and is deserving of the most serious attention on the part of the people. In the War of 1914-18 we had partial control, at immense cost, of the Atlantic, and were able to import from Chile. Shall we have control of the Atlantic, and will Chile be able to supply our needs, if we are so unfortunate as to be involved in another war? The assumption seems hazardous in the extreme.

There are some who hope to have seen the end of war. The situation at the present moment is a sad commentary on such hope. It cannot be safely assumed that we shall never again be compelled to resort to the arbitrament of the sword. The contingency is to be kept in mind. If the arguments for "key industries" are worth anything they apply with immense force to the nitrate industry. Of what conceivable use would dye-factories be without the materials for explosives and poison gas? Without nitric acid everything else is utterly useless. Even aeroplanes are futile without bombs. In 1917 the nations at war consumed over a million tons of combined nitrogen in the manufacture of explosives. Our own share of this was large. Can it be asserted that, in neglecting to make adequate provision for such supplies, the Government is justified in speaking of fostering key industries in any true sense at all?

We think it proper to say that we have no personal interests in any branch of the nitrogen industry, and are not engaged in urging the merits of any one process. It has been our aim to present the features of each branch of the industry in an entirely impartial manner, and we have had in mind the requirements of non-technical readers. Claims which we know to be without foundation have been ignored, and obvious defects of processes have not been kept out of sight. An impartial student of the industry cannot escape from the conclusion that all the processes which have been or are in use have serious defects. The arc process is clearly not suited, in its present form, to British conditions. The synthetic ammonia process, in the form used by the Badische company, is extremely complicated, expensive, and in many ways potentially dangerous. The cyanamide process (which is the one which could most safely be installed as an urgent war measure, since it has been thoroughly tried and tested) is cumbersome, and gives rise to large quantities of undesirable waste products, besides being economically less advantageous than the synthetic ammonia process. The remaining processes, particularly the Bucher process, which was so much boomed during the war period, have not answered expectations. It is inconceivable that further research should not lead to great, perhaps fundamental, improvements in the art of nitrogen fixation.

A beginning was made in nitrogen research during the War by the Nitrogen Products Committee of the Munitions Inventions Department. This was abandoned after the War, and any research which may now be in progress is done in secret by private firms. Can the Government rely on such work? Would the Admiralty be content to leave matters concerning naval construction and warfare entirely in the hands of shipbuilders and armament firms, without having a policy of its own, and without knowing what was being done? Why, then, should research on nitrogen fixation, which we have shown to be absolutely bound up with war policy, be entirely ignored? It would be useful if this question were asked in the proper quarter, and an enquiry made into the present position. The result of the enquiry would at least be interesting.

We have endeavoured throughout to assign credit for inventions and discoveries where credit is due. The claims of scientific research should be amply realised, and opportunities for such research, perhaps without obvious commercial possibilities, should not be limited by false ideas of economy. It may be that Sir Humphry Davy went a little too far in his statement that: "The mechanical and chemical manufacturer has rarely discovered anything; he has merely applied what the philosopher has made known, he has merely worked upon the materials furnished to him" ("Consolations in Travel; or, The Last Days of a Philosopher," 1829). In general, however, the tendency to error has been much too heavily weighted at the other extreme. It is time that the scientific investigator was given his due.

In conclusion we desire to acknowledge the assistance we have received from many sources in the preparation of the book. For the material for Plates I. to III., and much information, we are indebted to the Chilean Nitrate Committee. The Dorr Company kindly loaned the blocks for Plates IV. and V. Plates VI. to XVII. were reproduced from magnificent photographs supplied, with much useful information of a general character, by the Société Norvégienne de l'Azote, Christiania. The Stockholms Superfosfat Fabriks Aktiebolag supplied us, through Messrs. G. Boor and Co., London, with details of the new continuous cyanamide process of Carlson. Dr. E. C. Worden, of New York, gave us an account of his visit to the Knapsack works, and allowed us to make use of the account of the manufacture of nitric acid at Gretna contained in his "Technology of Cellulose Esters," vol. i., part 2 (1921), which may be referred to for a very detailed list of references to the literature of nitrogen products. Plates XVIII. and XIX. are reproduced, by the permission of the Controller of H.M. Stationery Office, from the pamphlet on "The Oxidation of Ammonia applied to Vitriol Chamber Plants," 1919. Messrs. Benn Bros. courteously allowed us to use the blocks for Figs. 9 to 16 from Mr. G. T. Calvert's excellent monograph on the "Manufacture of Sulphate of Ammonia and Crude Ammonia," of which they are the publishers, and to which, and to Lunge's "Coal Tar and Ammonia," readers are referred for a very full account of this industry. The Society of Chemical Industry sanctioned the use of the blocks for Figs. 1, 2, 3, 22, and 23, from publications in their *Journal*, to which reference is made in the text. The *Journal of the Society of Chemical Industry* (referred to in the text as *J.S.C.I.*) may be specially mentioned as containing articles and abstracts on all branches of the nitrogen industry. The *Journal of the Chemical Society* (*J.C.S.*) occasionally contains papers and abstracts of interest in this connection. Much useful information has also been found in the *Chemical Trade Journal*, which publishes weekly special articles dealing with the Chile nitrate and ammonium sulphate industries, and in the *Chemical Age*, which reports on the industry from time to time, and gives lists of patents.

A large amount of the statistical information contained in the book is derived from the now classical "Final Report of the Nitrogen Products Committee," published by H.M. Stationery Office in 1920, and from the "Statistical Supplement" to this Report, issued in 1921. These two documents contain more information, carefully and critically presented, than is to be found in any other source, and are worthy of the most careful study by anyone interested in the nitrogen industry.

Many other sources of information have been drawn upon to a smaller extent, and are referred to in the text. A large proportion of the material is, however, now published for the first time, and is based on the experience of the authors.

The index has been compiled by Mr. G. C. Attfield, B.Sc., who has also rendered valuable service in verifying the references to a large mass of data from the literature.

J. R. P.
L. H. P.

LONDON,
March, 1922.

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PART III

NITROGEN FIXATION PROCESSES

SECTION I

SYNTHETIC AMMONIA

THE nitrogen of the atmosphere over every square mile of the earth amounts to about 20,000,000 tons, or over thirty times the amount contained in the whole of the Chile nitre and by-product ammonium sulphate produced per annum. The supply is practically inexhaustible. The methods at present in use for fixing this atmospheric nitrogen are as follows:

I. The direct *synthesis of ammonia* from nitrogen and hydrogen gases (the Haber process): $N_2 + 3H_2 = 2NH_3$.

II. The direct *synthesis of nitric oxide* from the air in the electric arc, followed by the conversion of this into nitric acid and nitrates: (1) $N_2 + O_2 = 2NO$: (2) $2NO + H_2O + O = 2HNO_3$.

III. The reaction between nitrogen and calcium carbide, leading to the *production of calcium cyanamide*, $CaCN_2$, which can be used directly as a fertiliser or decomposed by superheated water with production of ammonia: (1) $CaC_2 + N_2 = CaCN_2 + C$; (2) $CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$.

IV. The conversion of ammonia, obtained by method (I.) or (III.), into nitric acid and nitrates by catalytic oxidation: $4NH_3 + 5O_2 = 4NO + 6H_2O$.

Each method has particular advantages and disadvantages, depending mainly on the particular facilities offered by any locality in the way of cheap power, fuel, and skilled labour.

The important process for the production of ammonia from the nitrogen of the air which depends on the direct combination of nitrogen with hydrogen, according to the equation $N_2 + 3H_2 = 2NH_3$, is usually called the "Haber process," since the scientific investigations which led to the establishment of the technical operations were mainly carried out by the German physical chemist Haber. The main discovery, relating to the influence of pressure, had, however, previously been made by Nernst. The materials required in the process are nitrogen and hydrogen gases. The production of nitrogen by the fractional distillation of liquid air has already been described, and a brief account will now be given of the manufacture of hydrogen.

The Manufacture of Hydrogen.

Apart from its application in the synthesis of ammonia from its elements, hydrogen gas is used in large quantities in the manufacture of margarine, candles, and hard soaps, from oils by so-called "fat-hardening" processes. Many liquid oils, when treated with hydrogen gas at a moderately high temperature in the presence of a catalyst, such as finely-divided metallic nickel, take up hydrogen to produce "saturated" compounds containing the maximum amount of hydrogen in the molecule of the fat (Sabatier and Senderens, 1897). These saturated fats are solids, and are free from the objectionable odours and tastes of the raw oils, such as whale oil.

Both for the preparation of synthetic ammonia and for the hardening of fats it is essential that the hydrogen gas should be in a very pure condition. The manufacture of hydrogen of a moderate degree of purity presents no great difficulties, and has been carried out for many years on the large scale. Such hydrogen has been used for filling balloons and for other purposes not requiring very pure gas. The economical production of pure hydrogen is a recent development of chemical technology, a brief account of which will now be given. For further details the reader may be referred to Greenwood's "Industrial Gases" (Baillière, Tindall and Cox, 1920), and to Rideal and Taylor's "Catalysis" (Macmillan and Co., 1919).

One method which has been used is the electrolysis of water. An electric current is passed through water to which an alkali or acid has been added. Hydrogen is given off at the negative pole, or electrode, and oxygen at the positive pole: $2H_2O = 2H_2 + O_2$. In practice a dilute solution of caustic soda and iron or nickel electrodes are used. Unless great care is taken, the resulting hydrogen is liable to be contaminated with oxygen, which mixes with it by diffusion, and if the proportion of oxygen is large the gas becomes dangerously explosive. Except in localities where electric power is cheap, as when it is generated from water power, the expense of this method is prohibitive. Large quantities of electrolytic hydrogen, however, are made as a by-product in the electrolysis of potassium salts in Germany, for the manufacture of caustic potash, and the power is obtained from lignite, and is therefore cheap. This gas is compressed into steel cylinders at 100 atmospheres or more.

The process most commonly used in England is based on the decomposition of steam by red-hot iron. A black oxide of iron and hydrogen are formed: $3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$. The process is reversible, and a large fraction of the steam passes on unchanged. The oxide of iron formed is reduced again to metallic iron by heating it and passing over it water gas, which is obtained by blowing steam over red-hot coke, and consists principally of hydrogen, carbon monoxide, and carbon dioxide. The hydrogen and carbon monoxide reduce the oxide of iron: $Fe_3O_4 + 2CO + 2H_2 = 3Fe + 2CO_2 + 2H_2O$. The iron is then heated again and steam blown over for the production of hydrogen. Several retorts are used, and each is "steamed" and "reduced" alternately in the manner described. The reduction of steam by heated iron evolves heat, whilst the reduction of oxide of iron by water gas absorbs heat.

In the Lane process spongy iron is contained in vertical iron retorts, heated to dull redness by gas firing, which are alternately traversed by steam and water gas. With careful working, hydrogen gas of 99·5 to 99·75 per cent. purity is obtained, the chief impurities being carbon monoxide and a little nitrogen from air leakage. The plants have capacities from 250 to 10,000 cubic feet of hydrogen gas per hour, and the cost of hydrogen on a pre-war standard was 4s. per 1,000 cubic feet, plus overhead charges.

In another set of processes the starting material is water gas, obtained by blowing steam through incandescent coke. This gas consists, as stated above, of a mixture of hydrogen, carbon monoxide, carbon dioxide, and impurities such as nitrogen (from air leakage, mainly accidental), and sulphur compounds such as sulphuretted hydrogen from sulphur in the coke. The approximate composition by volume is—

Hydrogen	49
Carbon monoxide	42
Carbon dioxide	4
Marsh gas	0·5
Nitrogen	4·5
Total	100

The reactions in the water-gas producer are principally three:

(1) $C+2H_2O \rightleftharpoons CO_2+2H_2$ (at lower temperatures, dull redness).

(2) $C+H_2O \rightleftharpoons CO+H_2$ (at high temperatures, bright redness).

(3) $CO+H_2O \rightleftharpoons CO_2+H_2$ ("water-gas equilibrium").

Carbon dioxide and sulphur compounds are removed by washing with water, preferably under pressure, and the main problem is then to remove the carbon monoxide. Several processes have been patented for this purpose, including the absorption of carbon monoxide in hot caustic soda solution; by absorption in dry calcium carbide heated to redness; by absorption in solutions of copper salts, such as cuprous formate; by the liquefaction of the carbon monoxide by strong cooling. The most promising method, however, is that patented in 1912 by the Badische Anilin und Soda Fabrik, of Ludwigshafen, Germany. In this, a mixture of water gas and steam is passed through a catalytic material such as a mixture of the oxides of iron, nickel, chromium, rare earths, etc., which is heated to 400° to 600° C. The carbon monoxide reacts with the steam, forming carbon dioxide, which is easily removed, and a further quantity of hydrogen from the steam: $CO+H_2O$ CO_2+H_2. This reaction is reversible; the best yield of hydrogen is obtained by working at fairly low temperatures. The whole apparatus is lagged, and the heat given out in the reaction is sufficient to maintain the catalyst at the requisite temperature. A small quantity of oxygen may also be added for the purpose of maintaining the temperature, but this is not necessary if the process is properly worked. Plants are constructed for this process up to a capacity of 35,000 cubic feet of hydrogen per hour, the cost (pre-war) being 1s. 9d. per 1,000 cubic feet.

The hydrogen obtained by the Badische process still contains ·1 per cent. or so of carbon monoxide, and is not sufficiently pure to be used directly for ammonia synthesis. Further purification is effected by scrubbing with hot caustic soda solution, and with a solution of cuprous formate in ammonia, in steel towers at 200 atmospheres pressure. The economical manufacture of hydrogen by this method was the key to the success of the synthetic ammonia process of the Badische Company, which is now worked on a gigantic scale (see p. 160).

Hydrogen is also formed as a by product in the manufacture of oxalic acid from sawdust, and in the manufacture of acetone by fermentation.

The Properties of Hydrogen.

Hydrogen is the lightest gas known; 1 cubic foot under ordinary atmospheric conditions weighs only about one-tenth of an ounce. Air is about fifteen times as heavy as hydrogen. The gas is used in filling balloons and airships. Hydrogen is combustible, and burns in air with a pale blue flame, forming water: $2H_2 + O_2 = 2H_2O$. When mixed with oxygen or air it explodes most violently in contact with a flame or spark. Hydrogen gas compressed to 100 atmospheres is sold in steel cylinders, painted red, and with a left-hand screw valve, so that they cannot be mistaken for oxygen cylinders. On account of its inflammable character, hydrogen is dangerous in airships, and it has been proposed to replace it by the completely inert gas helium, or a mixture of hydrogen and helium which is not inflammable. This was under consideration in Germany, in connection with Zeppelins, in 1913. On account of the great scarcity of helium the proposal came to nothing. The American authorities, who have made a thorough investigation of the matter, report that the cost of the helium would exceed that of the airship (see p. 5).

Synthetic Ammonia.

Although many experimenters have studied the problem of ammonia synthesis since the work of Regnault in 1840, success was not attained until Professor Nernst and Dr. Jost, and a little later Professor Haber and Dr. Le Rossignol, all working in Germany, tried the effect of increased pressure. This very soon led, in about 1905, to a workable process. It is noteworthy that all these investigators were "academic" chemists, and the researches were not at first undertaken with any idea of commercial application. Nearly all important commercial chemical discoveries have been made in this way. The real discoverers are in practically every case not technical chemists, and have no concern with the commercial exploitation of the processes. It is not asserted that this state of affairs is necessary; it is simply a fact that things are as stated. Another important source of successful technical processes is furnished by old and forgotten patents.

The laboratory work was so promising that in 1910 the problem was taken up by the great Badische firm, and with the intensive work of an army of chemists and engineers the manufacture of synthetic ammonia soon became a reality. Previous to 1905 the total weight of synthetic ammonia produced by all experimenters, from the time when it was discovered by Regnault about 1840, probably did not amount to more than 1 or 2 pounds. In 1920 the total capacity of the two German factories amounted to 1,500,000 tons of synthetic sulphate of ammonia. All this had been achieved in a space of less than ten years.

In the Badische process the operation is carried out at a relatively low temperature, say 500° C. (just short of a red heat), under pressures of about 100 to 200 atmospheres, in the presence of a catalyst which accelerates the reaction. Metallic iron, the very rare metal osmium, metallic uranium, molybdenum, and numerous other substances have been used as catalysts.

The amount of ammonia formed when the reaction comes to a standstill is greater the lower the temperature and the higher the pressure. In practice the temperature cannot be below 500° C., since otherwise the reaction becomes very slow even in the presence of a catalyst. The pressure is usually 200 atmospheres, although in the new process of Claude (see p. 167) pressures up to 1,000 atmospheres are used, whilst in the process of the General Chemical Company of America pressures as low as 50 atmospheres are specified.

Maxted has recently shown that at very high temperatures the yield of ammonia, after diminishing, again increases. By passing a mixture of hydrogen and nitrogen through an electric arc, a yield of 2 per cent. of ammonia was obtained. This result, which can be predicted theoretically, indicates the possibility of synthesising ammonia at the ordinary pressure by a method similar to that used for the manufacture of nitric acid from the air (see Section III.). The resulting ammonia could be removed from the gas, after cooling, by washing with water, and the gas circulated again and again through the electric arc. The great heat capacity of hydrogen as compared with air would indicate, however, that the power consumption would be very much less economical, and the danger of producing an explosive mixture by admixture of the gases with air would also be great. An advantage of the method would be that very pure hydrogen would not be required.

The equilibrium yields of ammonia under various conditions are given by Haber as follows:

Temperature in ° C.	*Volume per Cent. of Ammonia under Pressure of—*			
	1 *Atmosphere.*	100 *Atmospheres.*	200 *Atmospheres.*	1,000 *Atmospheres.**
300	2·18	52·1	62·8	—
500	0·129	10·4	17·6	—
536	—	—	—	40
607	—	—	—	30
672	—	—	—	20
700	0·0223	2·14	4·11	—
740	—		—	14
1,000	0·0044	0·44	0·87	—

The catalysts are usually mixtures of various substances. Metallic iron is the main constituent, but smaller amounts of other substances, called "promoters," are added. One of these is molybdenum. Uranium may also be used. Very pure iron, according to Nernst, has a very slight action only.

The German synthetic ammonia factories are situated at

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* From the experiments of Claude.

Oppau, near Ludwigshafen, and at Leuna, near Merseburg (Saxony).

The combined outputs during the war period of Oppau and Merseburg have been stated to be as follows (Statistical Supplement to Nitrogen Products Committee Report, 1921):

	Metric Tons of Ammonia per Day.		*Estimated Maximum Capacity in 1920.*
	1914.	1918.	
Oppau	25	220	250
Merseburg	nil	400	800 (when complete)*
Total ..	25	620	1,050

Assuming 95 per cent. continuous operation, the maximum annual outputs, calculated as metric tons of ammonium sulphate, from the German Haber factories are—

1914.	1918.	1920.
35,000	850,000	1,500,000*

The first turf on the site of the Leuna works was dug in May, 1916, and the works was completed in April, 1917. The main product is 20 per cent. ammonia liquor, although ammonium sulphate is made by the gypsum process (see p. 157) and ammonium chloride by the ammonia-soda process (p. 170). The consumption of fuel amounts to 11,000 tons of lignite per day, and 15,000 cubic metres of water are used per hour, 90 per cent. of this being recovered and used again.

The factory at Oppau was visited by representatives of the Allies, including Lieutenant McConnel, of the American Army, who has described his inspection in the *Journal of Industrial and Engineering Chemistry* for September, 1918.

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* Later information indicates that this figure for the Merseburg works has not yet been attained, and the maximum capacity did not reach 1,050 tons per day in 1920. The explosion at the Oppau works in 1921 (see p. 165) also reduced the total capacity of the German synthetic ammonia works (February, 1922).

During the year ending November 1, 1918, the works produced 90,000 long tons (of 2,240 pounds) of combined nitrogen, or ten times the estimated capacity of the new American synthetic ammonia plant at Sheffield, Alabama (see p. 186). This, with the reported production of 125,000 tons at Leuna, amounted to half the total annual output of combined nitrogen from Chile. The German Reichstag officially stated that 400,000 tons of combined nitrogen had been produced in 1916. The capacity at Oppau in 1918 was stated by Lieutenant McConnel to be as follows:

	Tons per Annum.	*Tons Combined Nitrogen per Annum.*
Ammonium nitrate	10,000	3,500
Sodium nitrate	130,000	21,400
Nitric acid	40,000	8,900
Ammonia	40,000	32,900
Total ..		66,700

The cost of the plant at Oppau is given as 5 to 10 million pounds sterling; the cost in America under present conditions would be 13 millions. The works employs 1,500 labourers, 3,000 mechanics, 350 clerks, and what will seem strange to the British commercial mind 350 expert chemists. It uses daily 1,750 tons of lignite, and 500 tons of coke, and the total cost of operation amounts to £11,000 per day.

The estimated cost of synthetic sodium nitrate made at Oppau is given as 0·87d. per pound, or 5½d. per pound of combined nitrogen. Natural Chile nitrate at 9s. per quintal is 1d. per pound in Chile, representing 6d. per pound of combined nitrogen. If all the ammonia made at Oppau were turned into nitric acid, the latter could be made at a cost not exceeding 1½d. per pound; the pre war price was 2½d. to 3d. per pound, and is now much higher (McConnel).

It is perfectly clear that the rest of the world is faced with a German industry which has entirely passed into the region of successful technical development. The production of vast quantities of synthetic nitrogen compounds by the Haber process is not, in Germany, a remote probability, but is an accomplished fact.

The actual working details of the Haber process are kept secret, but the broad outlines of the method are well known. The catalyst is contained in a series of say fifteen steel bombs, through which the mixture of carefully purified hydrogen and nitrogen, in the proportion of 3 to 1 by volume, is circulated under a pressure of 200 atmospheres. A system of heat-exchangers is used, so that the heat given out by the chemical reaction in the bombs is utilised in heating the incoming gas, and too great an elevation of temperature is avoided. The gases, after passing through a catalyst bomb, are cooled and washed with water under 200 atmospheres pressure to dissolve out the ammonia. The residual gas is dried, brought up to 200 atmospheres pressure, and passed through the next bomb, and so on. Fresh gas is added to make up the amount in circulation. The argon present in the nitrogen accumulates, and part of the gas has to be blown off to waste from time to time to prevent the argon rising above a certain amount in the gas. This would put an uneconomical load on the compressors, and would reduce the speed and yield of the reaction on account of the lowering in pressure of the active gases in the mixture.

The material of the bombs is important. If ordinary steel is exposed to hydrogen at a high temperature, the carbon is removed and the steel becomes rotted. Chrome steel, free from carbon, is used. Lining the bombs with pure electrolytic iron may also serve the purpose.

It has already been emphasised that the form in which ammonia is mainly used as a fertiliser is in combination with sulphuric acid as ammonium sulphate ("sulphate of ammonia") $(NH_4)_2SO_4$. In the manufacture of this salt, ammonia is absorbed in sulphuric acid, and part of the cost of the finished product is naturally that of the sulphuric acid required. This acid is made in most countries from iron pyrites, or to a less extent from sulphur, either native sulphur (increasingly in America, where there are large deposits) or sulphur recovered as a by product in the alkali industry (Chance-Claus process), or in the purification of coal gas "spent oxide" sulphur (see Partington's "Alkali Industry," Baillière, Tindall and

Cox, 1918). During the war the supply of sulphuric acid, which is used in immense amounts in the manufacture of explosives, ran short in the Allied countries, but the deficit was more particularly felt in Germany on account of the cutting off of part of the supply of pyrites by the blockade. The Badische Company, therefore, turned its attention to the replacement of the costly and scarce sulphuric acid by some cheaper and more abundant material. One such material is gypsum, a mineral form of calcium sulphate, $CaSO_4.2H_2O$, which is found in very large quantities. Gypsum is mainly used to produce plaster of Paris, by heating it to drive off part of the water. Experiments were made with the object of extracting sulphuric acid from gypsum, and although they were not very promising, a method of preparing ammonium sulphate from ammonia and gypsum instead of ammonia and sulphuric acid was successfully evolved. It was found that if finely powdered calcined gypsum, which is sparingly soluble in water, is suspended in a solution of ammonia, such as is obtained by washing with water the gas from the Haber plant, and a current of carbon dioxide is at the same time passed into the suspension, calcium carbonate (chalk) is precipitated and a solution of ammonium sulphate is formed. The solution is filtered and evaporated in vacuum apparatus. Carbon dioxide is formed as a by product in the manufacture of hydrogen from water gas, as previously described, The chemical reaction is-

$$CaSO_4+2NH_3+CO_2+H_2O=CaCO_3+(NH_4)_2SO_4.$$

This so-called "gypsum process" is of great importance, since it very materially lowers the cost of production of ammonium sulphate from ammonia. It is probable that it will have an important future in the synthetic ammonium sulphate industry.

The ammonium sulphate formed in this way is perfectly white and neutral, and represents the very highest grade of material which can possibly be made.

Wages and Power Costs in Germany.

Under pre-war conditions wages in German chemical factories were peculiarly variable: a 66-hour week was common, and the rate of pay for general labour was 0·65 mark per hour, or a weekly wage of 43 marks. Since the war an 8-hour day was fixed, and for similar labour the hourly rate rose to 1·7 marks, equivalent to a weekly wage of 81·6 marks—an increase in wages of 90 per cent. with a reduction in working hours of almost 28 per cent. If the same output per hour is assumed, the labour cost has risen 160 per cent. There was evidence, however, that the output per hour had fallen off in 1918, in many cases by about 25 per cent., so that the labour difficulties confronting industry are not confined to British conditions.

One of the most striking features of the growth of the chemical industry in Germany during the war was the apparently permanent value of much of the added plant and buildings. In this there is said to be a sharp contrast to British effort, nearly the whole of which had a purely temporary value, which has now disappeared. Full consideration appears, in fact, to have been given in Germany to the possible adaptation of buildings and plant to industrial conditions when the war demand had ceased.

An example of what is regarded as the typical German method is furnished by the Dormagen plant for the production of picric acid and T.N.T., belonging to the Bayer Company, and situated on the left bank of the Rhine a little way from Leverkusen, on the opposite side of the river. The buildings, which were begun late in 1916, are solidly constructed of brick and ferroconcrete, the sulphonating and nitrating houses *following in detail the general plan adopted as the standard for such work in the Bayer plants*. The nature of the buildings and the substantial and finished character of the plant are said to leave no doubt that "they are intended to be a permanent addition to the Bayer factories, and with very little alteration can be converted into a large installation for the manufacture of intermediates and dyes" (see J. Allan, *J. Soc. Chem. Ind.*, 1919).

Other eyewitnesses, however, merely state that in this factory "everything is done on a lavish, not to say unduly expensive and elaborate, scale" (Allmand and Williams, *loc. cit.*), so that the result is more probably due to slavish adherence to established routine, which is characteristic of most chemical engineers, rather than to any special far-sightedness on their part. The words italicised appear to support this view of the matter, which has not been given much prominence.

A valuable aid to the development of manufacturing processes in the Rhineland area is provided by the extensive deposits of brown coal (lignite) which occur somewhat removed from the river between Cologne and Crefeld. The ease of working these beds (there are similar deposits in Saxony) permits of power being obtained at very low costs, and there are several large power-stations situated in the lignite area, which in pre-war times distributed power to consumers at about $\frac{1}{5}$d. per unit, and are stated to be supplying power to-day at $\frac{2}{5}$d. per unit. This is very much lower than any price possible with coal in England.

The Stickstoffdünger Fabrik at Knapsack, manufacturing calcium carbide and cyanamide (see p. 209) in the brown coal area, formerly produced power at $\frac{1}{10}$d. per unit in its own power-station, but recent increased labour and material charges have increased the cost to the still very low figure of $\frac{3}{10}$d. per unit. An eyewitness remarks that "it is difficult to see how competition with these is to be met unless the projected central power schemes proposed for this country can distribute power at equally low rates."

The question of power costs is of basic importance in nitrogen fixation. The Haber plants at Oppau and Merseburg are spoken of by an eyewitness as "enormous in their dimensions, and a monument to the skill of the chemists and engineers who have erected them. Similar words may be applied to the plants at Höchst and Leverkusen, in which ammonia is oxidised to nitric acid (p. 278), and the imposing sight of the interior of the building at Höchst, which houses 256 platinum catalyst vessels with their various connections, is one which a chemist cannot easily forget. The capacity of this particular plant is 8,000 tons of nitric acid (100 per cent.) per month, so that approximately 1 ton of nitric acid is produced by each catalyst vessel per day. The whole installation, with its plant for vaporising ammonia, fans, catalyst vessels, absorbing towers, and nitric and sulphuric acid concentrating plants, is an outstanding example of the mass production policy which has been so largely adopted by the German chemical firms as a means of reducing production costs." The Höchst plant was, however, erected to supply war needs.

"A striking feature of this and very many plants for other purposes is that though in the aggregate the output is very great, the plants themselves consist of many units, each of which is a complete plant in itself, and enlargement of output is arrived at by erecting a fresh series of units rather than by increasing the size of the constituent part of the unit."

It is noteworthy in this connection that the laboratory experiments on ammonia oxidation made by the authors for the Munitions Inventions Department in England were based on just this principle: the size of unit employed in the laboratory was not far from the technical unit, and in later experiments was identical with it. Much ill-directed criticism on "the slight value of test-tubing to the chemical engineer" is the usual reward for their work to the research chemists. A great deal is often made of the gigantic difficulties facing engineers who are required to put a laboratory method into industrial operation. Very often the trouble lies in the attempt to diverge too freely from conditions which have been found in the laboratory to be essential, and to launch into ambitious modifications, which bring the process into familiar grooves, but take it out of the realms of practical realisation.

Synthetic Ammonia at Oppau.

The Oppau works was visited by commissions from a number of Allied countries, mostly for a few hours only. These earlier visits were followed by a second official mission in 1919, planned by the late Lord Moulton, who during the war was head of the Department of Explosives Supply. This official Government mission included the late Dr. Greenwood, who superintended the investigation of the Haber process in England, and four members of the staff of Messrs. Brunner, Mond and Company, who are developing the Haber process in England (see p. 178). This technical mission spent three weeks at Oppau; it met with some obstruction, but no doubt acquired a good deal of information of value, which has not, of course, been made public, although the expenses of the mission were defrayed largely from public funds.

From other sources, however, a good deal of information regarding Oppau has come to light. Mention may be made of the communication of one of the authors (*J. S. C. I.*, April 1, 1921), and some publications in America (*Chem. and Met. Eng.*, 1921). The Oppau plant evidently did not represent the last word in nitrogen fixation by the Haber process. Extremely careful regulation of pressures, temperatures, quantities of gas mixture, and purifying agents, were needed to control the manipulation of the complicated plant. Repairs and upkeep were heavy (see p. 186). It is said that in all over seventy explosions had occurred at Oppau since it started. During the first period, from 1914 to 1915, ammonia was said to cost only 2d. per pound, exclusive of interest, but including a small sum for depreciation. At that time, however, the lignite fuel cost only 8s. per ton, coke only 16s. per ton, common labour 3s. to 4s. per day, and skilled labour 5s. 6d. to 6s. per day. At the present time production costs are said to be three, and wages six, times these figures.

The Badische Company originally possessed a Leblanc soda works on the Ludwigshafen site, but this has long since been abandoned. The Ludwigshafen site is on the bank of the Rhine in the town of Ludwigshafen, facing Mannheim on the opposite bank. The Oppau factory is situated 3 kilometres further north on the same bank, and practically forms a continuation of the Ludwigshafen works.

In 1913, following work on a small experimental plant at Ludwigshafen, a synthetic ammonia factory was erected at Oppau, with a capacity of 20 tons of ammonia per day. This was increased to a capacity of 200 tons per day during the war. The Oppau works now deals exclusively with synthetic ammonia and its products.

The Leuna works, near Merseburg (Halle), was erected since 1916, and had in 1918 a capacity of about 400 tons of ammonia per day. (This is being extended to 800 to 1,000 tons per day.) The synthetic ammonia process has been associated with the ammonia-soda process, and the use of sulphuric acid in the manufacture of ammonium sulphate has been replaced by the production of this salt from ammonia, gypsum, and carbon dioxide (p. 157).

The number of workers employed at Ludwigshafen (for all purposes) during the war was 13,000 to 14,000, as against 8,000 to 9,000 previously; at Oppau 5,000 to 6,000 were employed during the war, and 3,000 in 1919. Communication with Oppau is by railway.

The combined capacity of Oppau and Merseburg in 1918, 210,000 tons of ammonia per annum, corresponds with over 800,000 tons of ammonium sulphate, or 1,050,000 tons of sodium nitrate, per annum, and is now sufficient to enable Germany to dispense entirely with Chile nitre. Other ammonium salts, such as the chloride and nitrate, and mixed salts for agriculture, are being put on the market. Oppau was said to have cost £15,000,000, and no expense has been spared on these plants, everything being on a most substantial and elaborate scale.

Description of Oppau. The power house generates 15,000 to 16,000 e.h.p., derived from lignite gas. The lignite is brought up the Rhine from the Ruhr district, and is used in the form of briquettes, 4 inches by 2 inches. (At Merseburg it is not briquetted.) "Bamag"* producers, 12 feet by 25 feet, with rotary grates, are used, only a little steam being added. From each kilogramme of lignite 3 cubic metres of gas (29 per cent. CO and 12 per cent. H) are obtained. Two parallel rows of producers and water-gas generators, 12 to 14 units in each row, are used. Each producer takes 20 tons of lignite and produces 2 million cubic feet of gas per day, representing about 18,000 kilowatts.

The water-gas generators use Ruhr oven coke, are 15 feet by 25 feet, of the Pintsch type with rotary grates, burning over 30 tons of coke and producing 3 million cubic feet of water gas per day. Some air is added, so that the resulting gas probably contains 18 per cent. of nitrogen.

The water gas is then treated in the Bosch hydrogen catalyst plant, consisting of 26 catalyst units in two sections of two rows of 6 to 7 units. Each unit comprises two heat-exchangers and one catalyst chamber, the latter elevated on girders.

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* "Bamag" = Berlin Anhaltischer Maschinenbau Aktien-Gesellschaft.

Each chamber has an oval cover with two 8-inch inlet pipes. The catalyst chamber is 16 feet by 12 feet by 10 feet deep, and probably contains two catalyst beds. The main exchanger is 30 feet by 6 feet; the other is half this height. The whole plant is lagged and autothermic working is possible. The issuing gas contains a few tenths of a per cent. of carbon monoxide. The catalyst was stated to be the same as that used in ammonia oxidation (p. 280), probably oxide of iron and chromium; it remains active for two years. The resulting gas is carried by a 3-foot main to the compression plant.

Before final compression the carbon dioxide is removed from the gas by washing with water in towers. The issuing water, which is circulated by pumps, passes through Pelton wheels, in which 60 per cent. of the power is recovered. The dissolved carbon dioxide is collected. There are eight steel towers, 30 feet by 4 feet, packed with rings. The water enters the top at 25 atmospheres, the gas, at a slightly lower pressure, being sent in at the bottom of the tower. The gas then passes through steel bottles to act as spray-catchers.

The gas is now compressed to 200 atmospheres, and passes to the plant for the removal of the carbon monoxide. This is effected by ammoniacal copper formate solution and by sodium hydroxide solution. Eight towers are used for the copper solution and eight for the soda solution, each 25 to 30 feet high, and 2 feet 6 inches external diameter, packed with Guttmann balls. The solutions are circulated by eight hydraulic pumps of special forged steel. The towers are also of special steel, in one piece, flanged at the ends. Vertical steel bottles are situated below the towers to act as liquid traps. The copper solution is then pumped down two 40-foot towers, and the carbon monoxide liberated is collected; the solution absorbs ten times its volume of gas, and the exact composition of the solution is important. The power used in this plant is 200 h.p.

The purified gas now passes by a high-pressure main to the catalyst plant, where the requisite amount of nitrogen from a Linde apparatus is added to make up to 25 per cent. in the gas.

The circulatory catalyst system comprises 15 units, each of

20 tons of ammonia per day capacity. About 6 per cent. of ammonia is formed, and the gas is then passed to the absorbers, where the ammonia is extracted under pressure by water. The total gas circulation is about 12,500,000 cubic feet reckoned as free gas.

The power for circulation is about 815 kilowatts. About 10 per cent. of the gas is lost by leakage. Argon and methane are allowed to accumulate to the extent of several per cent.

The Haber catalyst bombs consist of two straight sections of flanged Krupp steel forgings with a bolted flange in the centre. Each half is 19·7 feet long, the internal diameter is 31·4 inches, and the walls are 7·1 inches thick. The inside probably contains liners fitting closely to the main vessel and on the ends of which the covers make a gas-tight joint. There may be two further sheaths fitting loosely inside the liner, lined inside with refractory material. The space available for the catalyst is about 20 inches. The outer walls are heavily lagged and have a temperature of 300° to 400° C.; the temperature of the catalyst is probably about 600° C. The covers are held in position by fifteen studs of 4 inches diameter. The cost of each bomb exceeded 100,000 marks. Heat-interchangers of steel forgings, 19·7 feet long and 15 inches external diameter, fitted internally with $\frac{5}{8}$-inch tubes autogenously welded to tube plates, are provided.

Each catalyst bomb with its heat interchanger is mounted vertically in a separate compartment, the top of the bomb projecting a little above the latter. The compartments are of brickwork, closed by iron doors, with strong planking.

The starting appears to be done by admitting oxygen, which is not brought in contact with the catalyst. Electrical heating may also be used.

The catalyst consists of iron with a promoter. The presence of 0·01 per cent. of carbon monoxide in the gas is injurious.

The ammonia is removed from the gas at 200 atmospheres' pressure by scrubbing with water. Three water-injection pumps are connected with nine sets of absorbers. Each absorber consists of three steel spirals one above the other, the upper one being at a height of 60 feet. The gas is admitted to the lowest spiral, passing down this, then similarly through the other spirals. The water flows from the top to the bottom by gravity. Each coil is water-cooled, and a 25 per cent. solution of ammonia is obtained. Liquefaction of the ammonia by cooling is uneconomical.

The Oppau works was considerably damaged by a disastrous explosion on September 21, 1921, when a large number of workmen (about 1,000) lost their lives. The cause of the disaster is attributed to the explosion of a stock of 1,500 tons of fertiliser containing ammonium nitrate. The company were in the habit, it is said, of blasting this material when it had agglomerated, and the result might reasonably have been expected (see *J. S. C. I.*, 1921, p. 381R).

The Haber Process at Merseburg.

The process carried out at Merseburg differs from that at Oppau in two respects: (1) The mixture of nitrogen and hydrogen is made directly by treating a mixture of producer (air) gas and water gas, with the addition of steam, by the Bosch process; (2) the purified mixture of nitrogen and hydrogen, before passing to the main catalyst furnaces, is passed through a series of small catalyst furnaces ("Vorofen") to remove impurities.

There are thirty-one gas generators, five for air gas and the rest for water gas, all the air being provided by two blowers, each of 350 h.p. The gases are passed through three gasholders, each of 1,765,000 cubic feet capacity, providing a reserve for fifteen minutes. From these the gases are taken and mixed by blowers. The mixed gas then takes up the requisite amount of water vapour in two rows of six towers, each 82 feet high, through which hot water is pumped by seven pumps, each of 70 h.p. The water is warmed in a tower by the gases leaving the heat-exchanger of the contact furnaces for the hydrogen production. There are forty eight heat-exchanger towers.

The gases, containing hydrogen, nitrogen, carbon monoxide, and some carbon dioxide, now pass, after preheating, to two sets of twenty-four contact furnaces in which the reaction $CO+H_2O \rightleftarrows CO_2+H_2$ occurs. The gas passes to two gasholders, one of 350,000 cubic feet and one of 1,050,000 cubic feet capacity. Carbon dioxide is removed by washing with water in twenty-one to thirty towers at 25 atmospheres, the compression of the gas being in large part effected by one of the cylinders of the 200 atmospheres compressors, although a few pumps for 25 atmospheres are provided. Pelton wheels recover about 40 per cent. of the energy of the released gas, which power is utilised to compress water to 25 atmospheres. The power for this part of the plant is 40,000 h.p.

For the removal of the carbon monoxide, the gas, compressed to 200 atmospheres by twenty-four 1,000 h.p. compressors and twelve 500 h.p. compressors, is scrubbed in nineteen towers with ammoniacal copper formate solution circulated by nine double pumps of 600 h.p. The carbon monoxide recovered by reducing the pressure in towers is sent along with water to the hydrogen-contact plant. Six towers for caustic soda remove the remaining carbon monoxide, the soda being circulated by six small pumps.

The gas now passes to nine small contact furnaces ("Vorofen"), in which the remaining impurities are removed by catalyst mass before passing to the main contact furnaces. There are twenty-four main catalyst furnaces, five being in reserve, and twenty-four heat-exchangers. Circulation is effected by eleven pumps of 700 h.p. each ("Umlaufpumpen"). The ammonia formed is absorbed in water compressed to 200 atmospheres by five 100-h.p. and two 300-h.p. pumps, in twenty towers 39·3 feet high and 29 inches in diameter. The ammonia solution is passed to an expander, the ammonia gas evolved being absorbed in a separate tower. In the expansion the hydrogen and nitrogen gases dissolved in the water under 200 atmospheres pressure are liberated; these pass through the ammonia scrubbing tower and are collected in a gas-holder, from which they re-enter the circulatory system.

This completes our account of the Haber process for the synthetic production of ammonia as operated in the manner patented by the Badische Company. We shall next describe the exceedingly interesting and important modification of the process due to M. Georges Claude, the well-known French scientific inventor, and Director of the Société l'Air Liquide. This process is likely to become a formidable rival of the process as operated by the Badische Company, although it is not at present in use on a very large scale. A unit capable of producing 5 tons daily is at present in action (see "Nature," 1921, **107**, 765; *J. S. C. I.*, 1921, 420R).

The Claude Synthetic Ammonia Process.

In 1918 M. Georges Claude announced his invention of an improved synthetic ammonia process which has attracted widespread attention. It differs from the Badische process principally in operating under very much higher pressures. Pressures as high as 1,000 atmospheres are used, and the percentage of ammonia obtained in the gas is then 25, as compared with less than 6 in the Badische process. With this high percentage, simple cooling with water under the high pressure suffices to liquefy out most of the ammonia, which is thus easily separated from the mixture of residual hydrogen and nitrogen. From the liquid, ammonia gas is obtained by evaporation, and in this form it may be used in the ammonia-soda process, or be converted into nitric acid by oxidation. There is very little loss of pressure, as it is only necessary to circulate the gas three or four times over the catalyst, owing to the large amount of conversion on each circulation. The yield of ammonia amounts to 6 grammes per hour per gramme of catalyst, as compared with 0·5 gramme by the Haber process.

Very successful trials of the Claude apparatus were made on the experimental scale in Paris, and in June, 1919, the Société de la Grande-Paroisse was founded by the amalgamation of the Société l'Air Liquide and the Compagnie de Saint-Gobain, with a capital of 31 million francs. The Air Liquide Company placed at the disposal of the new concern the factory at Montereau, and the Claude process was tested there. One full-size unit is now in operation at Montereau.

In 1920 it was announced that the sole rights of the Claude process in Great Britain and Ireland, South Africa, the Commonwealth of Australia, New Zealand, and India, had been acquired by the Cumberland Coal, Power, and Chemicals Company, Ltd. As soon as the full size commercial unit at Montereau is in operation, it was stated, an English company, to be known as Atmospheric Nitrogen and Ammonia Products, Ltd., is to be formed, with a capital of £2,500,000. It is proposed that this new company shall erect a synthetic ammonia plant on ground adjoining the Allerdale Coke Oven Plant at Great Clifton, Cumberland. This site is within two miles of the port of Workington. The first unit of the synthetic ammonia plant will be of sufficient size to permit of the production of 50,000 tons of ammonium sulphate per annum. While there is every confidence in the merits of ammonium chloride, which is produced by a process patented by Claude and described below, as a fertiliser, it has not yet become established in British agricultural practice, so that the first product to be manufactured is to be ammonium sulphate, for which there is a ready market. A small plant is to produce ammonium chloride, and this material is to have a thorough trial as a fertiliser. The Cumberland Coal, Power, and Chemical Co. has recently acquired a controlling interest in the Tysse hydroelectric power station (145,000 e.h.p.), which produces power at $\frac{1}{25}$ of a penny per kilowatt hour, with factories at Odda, where it is proposed to make 156,000 metric tons of ammonium sulphate per annum.

A brief account of the peculiar features of the Claude process may now be given.

The improved synthetic ammonia process developed by Claude differs essentially from the development given to the original Haber process by the Badische Anilin und Soda Fabrik at Oppau, near Ludwigshafen, by aiming at increasing instead of diminishing the pressure at which the nitrogen and hydrogen enter into combination to produce ammonia. Both in Germany and in the United States the tendency has been to endeavour to bring about the combination at lower pressures rather than at higher pressures. The German original working pressure was some 300 atmospheres, and this has been reduced in present practice to some 200 atmospheres, while in the United States the General Chemical Company's modified Haber process has further reduced the pressure of combination to about 150 atmospheres or even lower. The relatively high temperature at which the process was originally worked has, however, remained unaltered at about 600° C., both in Germany and France. The French process, which is based upon original patents obtained by Claude entirely independent of those upon which the Badische Company rely, increases the pressure of combination to 1,000 atmospheres (14,000 pounds to the square inch) without reducing the temperature at which the combination is effected.

This pressure is reached in three main stages—viz.: 100 (by the aid of ordinary compressors), and then is at once brought to 300 and 1,000 atmospheres by special compressors so constructed that at the higher pressure they work freely and with little wear and tear. By thus increasing the pressure of reaction to 1,000 atmospheres the yield of ammonia is increased in practice to about 25 per cent., while the speed of reaction is commensurately increased. The power required to compress to 1,000 atmospheres is admittedly greater than to 200 atmospheres, but there are some essential advantages secured which in the final result make the total power expended per ton of synthetic ammonia produced no larger than that required for compression at 200 atmospheres.

Further advantages claimed are—

(1) In the French process conversion is effected in a single operation at 1,000 atmospheres instead of a lengthy chain of operations in the German process at 200 atmospheres, where that pressure has constantly to be maintained and restored at each step.

(2) In the French process the spontaneous condensation of the ammonia formed in the circulating gas is effected by ordinary cooling water at ordinary pressures, whereas the German method makes the use of injected water at high pressure (200 atmospheres) compulsory to ensure the re-entry of the uncondensed gases into the circulating mass at that pressure—as well as to make good the loss of pressure in the ammonia towers.

(3) The condensation of the ammonia in the French process is effected in a liquid condition, which provides a valuable source of refrigeration for the succeeding process of the fixation of the ammonia in a form suitable for agricultural use.

(4) The evaporation of the ammonia to a gaseous form, which in the original German process constituted an additional

source of expense, becomes entirely unnecessary with the French process, as the ammonia, being in a liquid form, passes of itself to the gaseous state without distillation.

M. Claude has from the outset appreciated the fact that the commercial success of the cheap production of synthetic ammonia necessarily depends upon its increased employment in agriculture. This in its turn depended upon its being linked up with a less expensive and more satisfactory method of fixing the ammonia for fertiliser purposes than can be secured by the manufacture of sulphate of ammonia, which necessitates the employment of sulphuric acid in large quantities (see, however, p. 157). He has devised a modification of the classical Solvay ammonia-soda process for the production of ammonium chloride and bicarbonate of soda, which consists in decomposing large quantities of sodium chloride (brine) with the aid of ammonia and carbonic acid gas. This results in the separation and precipitation on one side of ammonium chloride and on the other of sodium bicarbonate, when the alternate precipitation method due to Schreib is used, by means of which for each ton of fixed nitrogen in the form of ammonia 3 tons of bicarbonate of soda are recovered. The process may be briefly summarised as follows:

A saturated solution of common salt—*i.e.*, sodium chloride, NaCl, in water which contains about 36 parts of salt per 100 parts of water at the ordinary temperature, is saturated with ammonia gas. On passing carbon dioxide (carbonic acid gas, CO_2, obtained by burning limestone in kilns, or recovered in the hydrogen process, p. 163) into the ammoniacal brine under pressure decomposition takes place and ammonium chloride, NH_4Cl, and sodium bicarbonate, $NaHCO_3$, are formed:

$$NaCl + NH_3 + H_2O + CO_2 \rightleftarrows NaHCO_3 + NH_4Cl.$$

The reaction, which was discovered by two English chemists, Dyar and Hemming, in 1838, is reversible, and a state of equilibrium is reached when about two-thirds only of the salt are decomposed. The sodium bicarbonate is sparingly soluble in water, and even less so in a solution of common salt. It is therefore precipitated in the form of a white powder. The operation is carried out in towers or in closed iron tanks provided with cooling pipes through which cold water circulates. In the Solvay modification of this process, which is worked by Messrs. Brunner, Mond, and Company, the strength of the salt solution (natural Cheshire brine) is rather less than saturated, and under these conditions only sodium bicarbonate is precipitated, the ammonium chloride with one-third of the original salt remaining in solution. From this solution, obtained by filtration from the carbonated brine, the salt and ammonium chloride can be separated by crystallisation, and it is presumably in this way that the synthetic ammonium chloride is to be made by Synthetic Ammonia and Nitrates, Ltd. (p. 178). In the Claude process another modification of the ammonia soda process, due to Schreib, is used. By saturating the filtrate from the bicarbonate with common salt, adding a further quantity of ammonia, and again treating with carbon dioxide, ammonium carbonate, $(NH_4)_2CO_3$, is formed and ammonium chloride precipitated.

By further addition of carbon dioxide, ammonium bicarbonate is formed, which again precipitates sodium bicarbonate, and leaves ammonium chloride in solution:

$$NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl.$$

On the addition of more salt and ammonia, the cycle of operations is begun again, and the same solution may be used indefinitely. It may be noted that, if it is proposed to use the solution in this way, it will be necessary to add *solid* salt to bring it up to strength, and the evaporation of the strong brine, as obtained in this country, will add to the expense of the process. In the Solvay method no evaporation is required, the natural brine being used directly, but in this case it must be remembered that only one-third of the salt is usefully converted, and the rest is lost. It is a matter of economics which process will be cheaper in the long run.

The ammonium chloride obtained after two cycles in the Schreib-Claude process is said to be of 97 per cent. purity. The impurity is presumably common salt, which will not be prejudicial to many uses of the ammonium salt—*e.g.*, its application as a fertiliser.

It is stated that the fertilising value of ammonium chloride has been thoroughly investigated by M. Georges Ville, one of the leading experts in France, and found at least equal, for the same weight of nitrogen, to that of the sulphate. A similar result has been found by recent experiments in England. As the chloride is less weighty for the same weight of fixed nitrogen than the sulphate, the transport costs will be reduced.

In addition to the improvement in the manufacture of synthetic ammonia just described, M. Claude has described a new process for the manufacture of hydrogen from coke-oven gas. The latter contains about 55 per cent. of hydrogen, the rest being mainly methane, CH_4, a compound of hydrogen and carbon. The method described by Claude depends on the removal of the methane by washing the gas with solvents, such as ether, under pressure. The methane may be liberated again, and will serve for power purposes. It is claimed that this method will, when the plant is run in connection with coking works, lead to a reduction in the cost of hydrogen to at least half that of any previous method. With 200 coke ovens there would be enough hydrogen available in the gas to permit of the manufacture of 50,000 tons of ammonium sulphate per annum. The whole of the coke would then be available for sale, since it is not necessary to use coke in the manufacture of the hydrogen, as in the Badische process. It must be stated, however, that Claude's method of manufacturing hydrogen is still undeveloped, and many difficulties are likely to be experienced in its application on the large scale.

In a more recent patent, Claude describes the manufacture of hydrogen from purified or "stripped" coke-oven gas, containing ethylene, methane, hydrogen, and carbon monoxide. The gas is mixed with a little nitrogen, compressed and cooled in an ordinary liquefaction apparatus (p. 6). Nitrogen liquefies and washes out any carbon monoxide which has not deposited in the previous cooling, along with ethylene and methane. The cost is said to be 1s. 6d. per 1,000 cubic feet. The 2 or 3 per cent. of residual carbon monoxide is converted into methane by passing the mixture of hydrogen and nitrogen through a protector containing a little of the catalyst.

In order successfully to produce synthetic ammonia on a large commercial scale, considerable quantities of coal are required, and it is desirable that the manufacturing company should own its own coalmines and coke-oven plants, and that the works should be situated adjoining the collieries. After careful examination and study of coalfields in various parts of England, the conclusion arrived at is that West Cumberland offers the greatest advantages for such an undertaking, for the following reasons:

(*a*) Abundant supplies of suitable coal in close proximity to the seaboard.

(*b*) Large areas of land available for works.

(*c*) The existence of a harbour adjacent to the coal properties which can berth 5,000-ton boats, and can be readily made to accommodate steamers of a much larger capacity, which is extremely valuable for the import of raw materials and the export of the finished products.

(*d*) An ample water-supply for cooling and condensation purposes—a vital necessity in chemical product works.

Cumberland Coal, Power, and Chemicals, Ltd., own the share capital of collieries which have a capacity of about 2,400 tons of coal per day. There are installed on the collieries a total of 150 Kopper's modern coke ovens, with by product plants, the output of coke being about 800 tons per day. The coke-oven plant at Allerdale has been so laid out as to permit of a further fifty coke ovens being installed at a moderate expenditure, there being sufficient plant, etc., already installed to deal with the by-products from the extra fifty coke ovens. Four hundred and eighty acres of freehold land are being acquired, adjoining the coke-oven plant at the Allerdale Colliery, which site will be utilised for large synthetic ammonia works.

The company has also acquired control of about 20,000 acres of coal land, commencing at Maryport (Cumberland), running in a north-easterly direction. Two bore-holes are being put down on this area, one of which has reached a depth of 1,314 feet, and the other 1,060 feet. Both bore-holes are now in coal measures, and should shortly reach the various seams of coal that are being drilled for.

These details are based on a prospectus issued by the new company, which, since it contains several scientific inaccuracies (omitted or corrected in the above account), is obviously the work of the financial rather than the scientific interests. How far the extensive plans will be matured cannot be said, but of the great potential value of Claude's method there cannot be any doubt. Some further details of his process have been given by M. Claude himself.

The work of compression of a gas, at constant temperature, is proportional to the logarithm of the final pressure, starting from atmospheric. Thus, if the work of compression from 1 atmosphere to 200 atmospheres is 2·3, that from 1 atmosphere to 1,000 atmospheres will be only 3, or say 3·5, if allowance is made for the diminution of compressibility of a gas at high pressures.

At high pressures the percentage of ammonia in equilibrium is, as we have seen, considerably increased. Claude finds that the equilibrium yield can be raised from about 13 per cent. at 200 atmospheres pressure to over 40 per cent. at 1,000 atmospheres. A production of 5,600 to 6,700 grammes of ammonia per litre of catalyst space per hour, as compared with 350 to 400 grammes in the Badische process, has been attained. Whereas it is necessary, on account of the small conversion, to circulate the gases several times over the catalyst when working at 200 atmospheres, and to separate the ammonia formed between each separate conversion, it is sufficient to circulate three or four times only at 1,000 atmospheres. The volume of the apparatus, for the same production, is only about one-tenth that required at 200 atmospheres, on account of the greater reaction velocity at the high pressure.

The main source of difficulty in working at "hyperpressures" is the evolution of heat. This is twenty-five to fifty times that at 200 atmospheres, on account of the very much higher production of ammonia. The difficulty is then, not to conserve the heat, as is the case in the Badische process, but to get rid of the surplus heat. This problem, according to Claude (*Revue scientifique*, May 28, 1921), has been overcome in the semi-technical unit operating at La Grande Paroisse, which produces 1·25 metric tons of ammonia per day, and has also approached solution in the unit for 5 tons per day, which is operated by a compressor bringing 700 cubic metres of mixed gas to 1,000 atmospheres per day.

The percentage of ammonia in the mixture after passing the catalyst is approximately proportional to the pressure. The partial pressure of the ammonia is therefore roughly proportional to the square of the pressure. It is 250 atmospheres in a mixture containing 25 per cent. of ammonia at 1,000 atmospheres, as compared with at most 12 atmospheres in the 6 per cent. mixture at 200 atmospheres obtained in the Badische process. The vapour tension of liquid ammonia at the atmospheric temperature is from 7 to 8 atmospheres, which is negligible in comparison with 250 atmospheres, but by no means so in comparison with 12 atmospheres. It is therefore sufficient to cool the gas obtained in the Claude process in a coil immersed in water to condense out most of the ammonia in a liquid state, whilst in the Badische process it is necessary to resort to washing with water under 200 atmospheres pressure to recover the ammonia. To expel the ammonia as gas from the solution in water requires the expenditure of fuel, whereas in Claude's process the liquid is allowed to evaporate spontaneously, producing cold which can be utilised in the apparatus liquefying the air for the production of nitrogen, or in the fixation of the ammonia.

M. Claude remarks characteristically: "D'ailleurs, tous les goûts sont dans la nature, et si la Badische Anilin met son point d'honneur dans la complexité et dans l'énormité des choses qu'elle a realisées, j aime mieux, et c'est mon ambition, mettre le mien, un jour prochain, dans la maniabilité et dans la simplicité de mes engins. Ce sera, je crois, plus français."

Synthetic Ammonia in England.

It will now be profitable to consider briefly what steps have been taken by nations other than Germany to develop the manufacture of synthetic ammonia. We may commence with the situation in England.

Before and during the early stages of the Great War nothing was heard of synthetic ammonia in England, although the process and its possibilities were known to all English chemists conversant with the recent progress of the science. Dr. Le

Rossignol, who was largely concerned with the experimental development of the Haber work, and is named in some of the patents, is a British subject. During the war the importance of the process became evident, and experiments were carried out for the Munitions Inventions Department of the Ministry of Munitions. The Nitrogen Products Committee, under whose direction the experiments were made, was set up on the initiative of the Faraday Society, the president of which was at that time Sir Robert Hadfield, F.R.S., whose interest in scientific research is well known. The general direction of the research was in the hands of Dr. J. A. Harker, F.R.S., the work with synthetic ammonia being entrusted to Dr. H. Greenwood, formerly a research student with Haber at Karlsruhe. In the course of this work, which lasted until the Armistice, considerable improvements were evolved in the method of production of synthetic ammonia, and a laboratory plant was in operation at University College, London, with success. The outcome of this work was intended to find application on a large scale during the war, since at one time there were serious doubts as to the possibility of maintaining an adequate supply of nitrates from Chile. The duty of putting into practice the results achieved in the laboratory was entrusted to the Explosives Supply Department, the distinguished head of which was the late Lord Moulton. The plans of the National Factory were to be drawn up by Mr. K. B. Quinan, the technical adviser of Lord Moulton. Mr. Quinan had, unfortunately, no theoretical or practical knowledge of the fixation of nitrogen, and for other reasons nothing had been done at the time of the Armistice beyond the acquisition of the site at Billingham-on-Tees, admirably exposed to Zeppelin attack, and the purchase of some plant.

On May 2, 1918, Mr. Kellaway, in reply to a question in the House of Commons by Sir W. Beale, stated that the Haber process (presumably the Badische process) was protected by British patents which, as in the case of similar patents, were vague as to the fundamental factors necessary for the commercial exploitation of the process. The exact knowledge existing in this country was then, it was stated, entirely insufficient to justify commencing the erection of manufacturing plant without extensive research. Modifications of the patents had been made and protected by Departmental patents in the names of the Research Staff, or the Controller of Munitions Inventions, and assigned to the Secretary of State for War. The process and modifications so protected had not been used by British manufacturers for actual production as distinguished from laboratory investigations, since the research work, which had been conducted unremittingly since July, 1916, had then only just reached a stage at which it was considered possible to proceed from the laboratory to the manufacturing scale.

This date—viz., May, 1918 therefore marks the time when operations were commenced in England to put the synthetic ammonia process on a technical scale.

In view of the importance attached to the modifications made in the process, and the probable utility to the enemy of these modifications, Mr. Kellaway continued, the results of the research work had not been made public, since such information could only be of value to those desiring to erect a large Haber plant. This information could be communicated confidentially if proposals for the erection of a plant were put forward, and the financial arrangements approved by the Treasury. Mr. Kellaway further announced that the Explosives Department was then engaged in translating the research work into large scale operations. Conferences were being held between the Ministry of Munitions, the War Office, the Board of Trade, the Admiralty, and other Departments, with a view to determining how far and in what manner the results of the general research work of the Munitions Inventions Department could be placed at the disposal of manufacturers of this country for the benefit of the nation as a whole.

The manufacture of nitrates was so obviously a "key industry," and so closely connected with the safety of the nation in war and its prosperity in peace, that it was expected in most quarters that the work of the National Factory would have been carried on after the Armistice, as has been the case in America. The research workers had transferred their rights to the Secretary of State for War, and it was not contemplated that these rights should be "communicated confidentially" to private firms trading for profit, even if the "financial arrangements " were " approved by the Treasury," unless some drastic revision of the terms of the agreement entered into by the inventors, under the pressure of war conditions, should be made.

In April, 1919, a somewhat grandiose announcement appeared in the Press to the effect that " the fixation of atmospheric nitrogen is about to be undertaken in earnest, under such conditions and auspices as will ensure its immediate and vigorous prosecution on a scale commensurate with its supreme importance for the safety of the country in war and its prosperity in peace." These auspices were as follows: " A syndicate comprising Messrs. Brunner, Mond, and Company, Ltd., and Explosives Trades, Ltd., had purchased the extensive site at Billingham-on-Tees, in the county of Durham, acquired by the Government during the war for the purpose of building thereon a nitrogen fixation factory. A special staff of engineers and chemists had been engaged for some months in designing the details and general arrangements of the proposed plant and in working out the many difficult problems inherent in the process." The article very properly points out that " the overwhelming necessity for establishing nitrogen fixation within our own borders is proved beyond question. Until that is done we shall remain in a position of the greatest insecurity." It is sad to reflect that we are still in this position of greatest insecurity, more than three years after the technical experts had begun their work " in earnest "—doubtless this phrase was intended to differentiate their labours from those of the Government inventors.

Another year passed, and in 1920 it was announced that "Synthetic Ammonia and Nitrates, Ltd.," had been formed by Messrs. Brunner, Mond, and Company (Explosives Trades had now apparently withdrawn), with a capital of £5,000,000, to take over from the Government the manufacture of nitrogen products from atmospheric nitrogen and to develop this manufacture on a commercial scale. By agreement with the Government, it is stated, the company will always be under British control, the directors are to be British born, and the first directors are to be approved by the Government. The works will be situated on the site purchased from the Government at

Billingham-on-Tees. and it was proposed to erect at once a plant for the production of 100 tons of ammonia per day (this is now apparently reduced to 20 tons per day). with provision for a rapid extension to 300 tons per day. equivalent to 150,000 tons. rising to 450,000 tons, of ammonium sulphate per annum (*cf.* the figures for the German works. p. 154). The chief product. however. will be ammonium chloride. which will be manufactured simultaneously with sodium carbonate, and it is hoped that the agricultural community will eventually adopt this form of fertiliser. thereby enabling it to obtain supplies of fertilisers at a reduced cost. It may be noted at this point that ammonium chloride is a by-product of the ammonia-soda process. Explosives Trades, Ltd., had undertaken to purchase its requirements in ammonia from the company, and to erect plant to the extent desired by the Government for its conversion into nitric acid and explosives by oxidation. The technical staff of the Company had made a thorough inspection (presumably with Allied sanction) of the works at Oppau in Germany (p. 160). which had produced at the rate of 250 tons of ammonia per day; of the nitrogen plant belonging to the United States Government at Sheffield, Alabama, and of the General Chemical Company's plant at Laurel Hill, New York; also of the Claude experimental plant at La Grande Paroisse. The experimental plant of Maxted, of Gas Developments. Ltd., Walsall. and all relevant information and patents. had been purchased. The process selected, it is stated, is a modified Haber process. worked out entirely without German assistance (Dr. Greenwood, it may be recollected, was a former pupil of Haber in Germany). All enemy patents bearing on the process have been placed by the Government at the company's disposal. and the royalties on these will be paid to the Custodian of Enemy Property for account under the reparation clauses of the Peace Treaty.

It is of interest in this respect to note the recommendation of the Minister of Munitions as the outcome of a delegation from the Nitrogen Products Committee on March 15, 1917, which met him to discuss matters arising out of their interim report. At that time the only process on which definite information, capable of translation into large-scale working, was available as a result of research work carried out for the Ministry was the oxidation of ammonia. The Minister, among other matters, decided that "the information resulting from the research work was to be placed freely at the disposal of *bona-fide* manufacturers, but was not to become the property of any one firm or group of firms."

It is perhaps necessary to add, by way of conclusion, that not one of the actual inventors, whose patents were taken out during the war and assigned to the Secretary of State for War for national use, has received any reward or benefit for his work.

Synthetic Ammonia in France.

We may turn now to the activities of France. During the war researches on the synthetic production of ammonia were carried out in France with aims similar to those undertaken by the Munitions Inventions Department in this country. The two groups of research chemists were in close touch. The results were, however, in a less advanced stage at the time of the Armistice than was the case in England. In 1920 it was stated that the firm of Kuhlmann, in conjunction with colliery companies at Lens and the Bank of Paris, had acquired the patent rights for the Haber process. A capital of 50,000,000 francs is to be invested in the process. In the same year a statement by the French Government appeared, to the effect that on November 11, 1919, the French Minister of Industrial Reconstruction (M. Loucheur) had signed a convention with the Badische Company of Germany, with the object of obtaining their assistance in regard to the technical details necessary for the economical working of the Haber patents owned by that company, but acquired by the French War Minister under the Peace Treaty. As the period under which the convention could be denounced had then elapsed (viz., at the time of the announcement in 1920), the agreement came into force on April 1, 1920, and a Bill intended to carry it into effect was placed before Parliament. The Bill provides that the French Ministers of War and Finance can jointly concede the benefits accruing from the convention to a French individual or company, or, failing that, to the Compagnie Nationale de l'Azote, in trust on behalf of the State, such company to be assigned a suitable portion of the National Powder Factory at Toulouse. A credit of 10,000 francs will be opened in order to provide for the initial cost of applying the convention.

We have described the entirely novel and independent modification of the Haber process due to the French inventor, M. Georges Claude. This is probably the most important discovery made on the Allied side. It may also be mentioned at this point that Professor Matignon, in 1918, stated as his opinion that the patents of Haber were invalid, on account of previous publications. These comprise patents by Tellier of 1865 and 1881; of Tessié du Motay in 1871, of Ramsay and Young in 1884, of La Christiania Minekompani in 1896, and of Le Chatelier in 1901. The published work of Perman also includes statements as to the reversibility of the reaction and to the catalytic effect of metals.

The Haber and Claude processes have been investigated by a commission. The results are not to be published, but it is understood that a decision in favour of the Claude process has been reached (October, 1921), since the Compagnie Nationale de l'Azote, which owns the French rights of the Haber patents, will be liquidated shortly. If this is so, the manufacture of synthetic ammonia in France will be confined to the Société de la Grande Paroisse, which uses the Claude process.

Synthetic Ammonia in America.

In America the Haber process was modified by some experiments carried out by the General Electric Company of New York. In their process very large catalyst chambers of chrome steel or other suitable alloy are used, and the catalyst is composed of cobalt (59 parts) and sodium (69 parts), treated with ammonia gas at 300°. The operation is carried out at 520° to 540°, under the relatively low pressure of 80 to 90 atmospheres. In February, 1920, it was announced that the General Chemical Company of New York and the Solvay Process Company of Syracuse, N.Y., had jointly undertaken the organisation of a new company, called the Atmospheric Nitrogen Corporation, to develop nitrogen-fixation processes. The capital is 5,000,000 dollars, and a plant is to be erected at Syracuse at an estimated cost of 1,000,000 dollars. It may be mentioned that the Solvay Company has intimate relations with Messrs. Brunner, Mond, and Company.

In Italy it is announced (May, 1920) that an American subject has obtained concessions from the Government to utilise 800 h.p. from the waterfalls of Terni, seventy miles from Rome, and has taken over a munitions plant for the synthetic production of ammonia. Electrolytic hydrogen is used, with a pressure of 250 atmospheres, and one unit of twelve is said to be in operation.

Nitrogen Fixation in the British Empire.

The following brief account of projected nitrogen-fixation processes within the British Empire was made available through the courtesy of Dr. J. A. Harker, F.R.S., of the Munitions Inventions Department (1920):

Among the terms of reference of the Nitrogen Products Committee was the following:

> "To consider the relative advantages for this country and for the Empire of the various methods for fixation of atmospheric nitrogen from the point of view both of war and peace purposes; to ascertain their relative costs, and to advise on proposals relevant thereto which may be submitted to the Department."

Since the Armistice a number of the schemes, of which the Nitrogen Products Committee previously had details, but which had been suspended because of the war, have again been taken up, and, in addition, a certain number of new ones have been initiated. The schemes on foot within the British Empire of which we now have some information are about twenty in number, although it is by no means certain how many of these are likely to proceed. They are located in Canada, Labrador, British Columbia, Newfoundland, Australia, New Zealand, Tasmania, Upper and Lower Egypt, Natal, the Transvaal, West Indies, India, and Ceylon. In addition, there is a probability of British capital and plant being employed in three or four others on foreign territory. A number of the schemes are of a purely local character, and are designed mainly for the supply of fertiliser or other chemical product to inaccessible areas, where importation is either uneconomic or impossible by reason of lack of transport facility. In most cases the schemes would meet new demands rather than compete with existing sources of supply. As part of many of the schemes it is proposed to develop hydro-electric power, the whole or a portion of which is to be used in the manner suggested. The products it is proposed to make include ammonium sulphate, both synthetic and by-product, cyanamide, nitrate of lime, nitrate of soda, and sodium cyanide.

It may be of interest to give as examples further details as to one or two of these. One, which at the present moment is being actively proceeded with, is the project relating to the manufacture of fertiliser in Egypt, employing water power to be developed at the great Dam of Assouan. A firm of British engineers were asked, in 1919, by an influential Anglo-Egyptian group of capitalists, to elaborate a project whereby the hydro-electric power obtainable from the Dam should be developed and applied to the local requirements. Under this scheme it is proposed to develop the whole of the power available. The bulk of this is of a seasonal character, owing to the peculiar conditions prevailing in the Nile valley, and throughout the year it is impossible to rely on more than 10,000 continuous kilowatts. This continuous power will be used for irrigation purposes to bring under cultivation a wide area of land at present useless. During the flood period the quantity of power available is increased to about 65,000 kilowatts, and it is proposed to devote the additional power, for a period of about seven months annually, to the manufacture of about 25,000 tons of nitrate of lime, by an entirely new form of the arc process.

A second project now rapidly developing relates to the west coast of Newfoundland, where a hydro-electric installation for over 100,000 h.p. is projected for nitrate of lime and paper-pulp manufacture, with possibly some cyanamide. This power development is one of the very few possessing the necessary local advantages, and at the same time large and cheap enough to justify the employment of the arc process.

In Natal coal is available at the present day in large quantity at 2s. 6d. to 3s. a ton, and a carbonisation scheme, directed mainly to ammonia recovery, is now under active discussion.

The manufacture of cyanide in the South African goldfields is also contemplated.

Cost of Synthetic Ammonia.

The economics of synthetic ammonia have been carefully studied by the Nitrogen Products Committee. Assuming that pure hydrogen can be made at a cost of 2s. 6d. per 1,000 cubic feet, which was considered ultimately possible, the calculations of the Committee lead to a figure of £17 per metric ton of synthetic ammonia made by this process, or £20·64 per metric ton of fixed nitrogen. This estimate is based on the following items:

	Ammonia per Metric Ton. £.	*Percentage of Total Cost.*
(*a*) Hydrogen: 77,000 cubic feet at 2s. 6d. per 1,000 cubic feet, inclusive of compression and of all working costs and depreciation of hydrogen section	9·625	61·6
(*b*) Nitrogen: 26,000 cubic feet at 6d. per 1,000 cubic feet, inclusive of all working costs and depreciation of nitrogen section ..	0·650	4·2
(*c*) Wages (other than for gas plants)	0·234	1·5
(*d*) Power for compressing nitrogen and for heating, catalysts, 1,500 kilowatt-hours, at 0·25d. per kilowatt-hour	1·562	10·1
(*e*) Repairs at 10 per cent. on catalyst section ..	1·000	6·4
(*f*) Superintendence	0·060	0·4
(*g*) General expenses	0·300	2·0
(*h*) Fixed charges	0·300	2·0
(*i*) Depreciation at 10 per cent. on catalyst section	1·000	6·4
(*j*) Depreciation and repairs at 10 per cent. on remaining plant, buildings, etc.	0·840	5·4
Total ..	15·571	100·0

The addition of 5 per cent. interest on a capital cost of £40 per metric ton of ammonia per annum brings this up to £17·57 per metric ton of ammonia. The Committee believe, however, that the actual cost, exclusive of this interest, would work out at about £17 per ton of ammonia.

The above figures show that over 60 per cent. of the cost of fixation of nitrogen by this process is represented by the hydrogen. Although the power required is by no means negligible, representing as it does some 10 per cent. of the total cost at the low figure of 0·25d. per unit, it is small in comparison with that used in other fixation processes, such as arc and cyanamide, which include electric furnace operations. This low power consumption in the synthetic process is, however, largely illusory. In the manufacture of hydrogen by electrolysis, large amounts of energy are absorbed, and in the production of hydrogen by reduction processes, or from water gas (p. 149), considerable amounts of coal are used. This coal is potential energy, which could be utilised in other fixation processes, and the hydrogen item in the synthetic ammonia balance-sheet really corresponds with the energy item in the arc process. On the other hand, in the cyanamide process (see *ante*), not only is a good deal of electrical energy used, but also considerable amounts of carbon (potential energy) in the form of electrodes, and in chemical combination in the cyanamide. All this carbon is ultimately wasted.

The production of large quantities of hydrogen containing a maximum of 0·05 per cent. of carbon monoxide and less than 1 part per million of sulphur compounds, such as is required in the synthetic method, is a process not hitherto carried out on a commercial scale in the United Kingdom. The water-gas catalytic process (Badische process) is regarded as the most promising source of this hydrogen, although this process has not been successfully operated on a large scale outside Germany. Large-scale trials in America broke down in some essential details.

Some figures for the German works have been published by Lieutenant McConnel, and he has made the following calculations on the cost of production of synthetic fixed nitrogen at that factory (*cf*. p. 154).

The estimated costs of production at Oppau, which he states were given him by the general manager, are as given on p. 186.

The plant is operated continuously. Probably under normal conditions it is shut down 10 per cent. of the time for repairs. The total cost per day is then $58,337. The assumed output is 553,000 pounds of fixed nitrogen per day. The cost of fixed nitrogen is, therefore, \$58,337 ÷ 553,000 = 10·55 cents per pound, equivalent to 1·74 cents per pound of sodium nitrate. If the ammonia produced were oxidised, the existing plant for this would have to be increased threefold, and the cost of fixed nitrogen as nitric acid would be 12 cents per pound of nitrogen, equivalent to 2·68 cents per pound of nitric acid, or about 3 cents per pound of concentrated nitric acid. The pre-war price of nitric acid from Chile nitre was 5 to 6 cents per pound, and is now materially increased.

Lignite for producer-gas engines ..	400	tons per day.
,, ,, steam to hydrogen plant	1,000	,, ,,
,, ,, steam-power plant ..	350	,, ,,
Total ..	1,750	,, ,,
Coke for water-gas producers ..	500	,, ,,

Operating costs per day:	\$	
1,500 labourers at \$1.40 ..	2,100	
3,000 mechanics at \$2.25 ..	6,750	
350 clerks at \$3.25	1,137	
350 chemists at \$3.50 (?) ..	1,050 (?)	\$
		11,037
Fuel:		
1,750 tons of lignite at \$4.00 ..	7,000	
500 tons of coke at \$8.00 ..	4,000	
		11,000
Interest:		
\$50,000,000 at 6 per cent.		8,000
Maintenance and renewals at 10 per cent. ..		14,000
Overhead, taxes, pensions, etc., say		10,000
Total cost per day ..		54,037

"Metallurgical and Chemical Engineering," 1920, p. 841, gives the figures for the No. 1 Nitrate Plant at Sheffield, Alabama, which used a modified Haber process. This was not a success. It is anticipated that developments will take until 1924, and possibly 25,000 tons of nitrogen may be fixed per annum in 1930. An additional cost of \$20,000,000 will be required. The items in the cost of the plant as it stands are:

	\$
Ammonia plant	5,592,000
Nitric acid oxidation plant	2,184,000
Ammonium nitrate plant..	386,000
Power plant	1,552,000
Land and buildings	1,406,000
Village for workpeople	1,852,000

The above figures show that over 60 per cent. of the cost of fixation of nitrogen by this process is represented by the hydrogen. Although the power required is by no means negligible, representing as it does some 10 per cent. of the total cost at the low figure of 0·25d. per unit, it is small in comparison with that used in other fixation processes, such as arc and cyanamide, which include electric furnace operations. This low power consumption in the synthetic process is, however, largely illusory. In the manufacture of hydrogen by electrolysis, large amounts of energy are absorbed, and in the production of hydrogen by reduction processes, or from water gas (p. 149), considerable amounts of coal are used. This coal is potential energy, which could be utilised in other fixation processes, and the hydrogen item in the synthetic ammonia balance-sheet really corresponds with the energy item in the arc process. On the other hand, in the cyanamide process (see *ante*), not only is a good deal of electrical energy used, but also considerable amounts of carbon (potential energy) in the form of electrodes, and in chemical combination in the cyanamide. All this carbon is ultimately wasted.

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SECTION II

THE CYANAMIDE PROCESS

WE shall now give an account of the second important method of nitrogen fixation viz., the cyanamide process. This is much better known in its working details than the Haber process, and is extensively used in Allied and other countries as well as Germany.

This process for the fixation of atmospheric nitrogen, which rivals the Haber process and has already found extensive and successful application, was discovered by the German chemist F. Rothe. In it the raw materials are lime, coke, and nitrogen. By heating a mixture of lime and coke in the electric furnace to 3,000° C., calcium carbide, CaC_2, is formed: $CaO+3C=CaC_2+CO$. This material is well known as a source of acetylene gas. If the carbide is cooled, crushed, and heated to about 1,100° C. in a stream of pure nitrogen, absorption of the gas occurs, with the formation of a mixture of graphite (carbon) and *calcium cyanamide*, $CaCN_2$. It is not possible to carry out this reaction directly by passing nitrogen over the fused carbide in the electric furnace, since the reaction, $CaC_2+N_2 \rightleftharpoons CaCN_2+C$, is reversible, and takes place in the opposite direction at very high temperatures.

The crude mixture of calcium cyanamide and graphite is ground to a powder, and the product, which is dark grey in colour, is known as "nitrolim." When treated with a little cold water, unchanged carbide is decomposed, with evolution of acetylene, and the dry powder may then be used as a fertiliser. When a mixture of cyanamide and water, after the addition of a little soda, is heated by steam under pressure in closed steel boilers ("autoclaves"), ammonia is formed: $CaCN_2+3H_2O=CaCO_3+2NH_3$. The mixture is agitated by stirrers, and the ammonia gas allowed to pass out, mixed with a good deal of steam, to a rectification column or still (p. 115), from which a solution of ammonia in water, or ammonia gas, according to the conditions, is obtained. The ammonia may also be received in sulphuric acid, when ammonium sulphate is formed (*cf.* Partington, "Alkali Industry," p. 203).

This is, briefly, the principle of the cyanamide process. The method is in use on an increasing scale in France, Germany, America, Italy, Norway, Sweden, and Japan. It is therefore an established process, and the working details are thoroughly well known. Many improvements have recently been introduced.

Calcium Carbide.

The most important intermediate material in the manufacture of cyanamide is calcium carbide, and a few words may be said on the manufacture of this substance. Since calcium carbide may become the starting-point in the manufacture of synthetic alcohol and acetic acid, both products of very great importance in many industries (particularly in that of cellulose products for various uses), it is evident that the manufacture of calcium carbide is a process which has interests beyond those which it is proposed to describe in the present volume.

The modern process for the manufacture of calcium carbide dates from some purely scientific researches of the great French chemist Henri Moissan, the discoverer of fluorine and of artificial diamonds. Moissan was engaged in investigations at very high temperatures, which ultimately led to his artificial production of diamonds from charcoal. In the course of this work he made use of the extremely high temperature of the electric arc, discovered early in the last century by Sir Humphry Davy. When two rods of carbon, connected with the poles of a powerful battery or dynamo, are brought in contact and then separated by a short distance, an arc of flame appears between the points of the rods, which is the source of light in the familiar "arc lamp." This arc has an extremely high temperature, at least 3,000° C., and this was utilised by Moissan in his electric furnace. The arc is produced inside a chamber of lime, a very refractory material.

Moissan found (1892) that, in the electric furnace, a mixture of lime and carbon is converted into calcium carbide: $CaO+3C=CaC_2+CO$. This discovery was made almost simultaneously

(1893) by Willson in America, and before long the manufacture of carbide was carried out on the large scale by the use of electric power from Niagara Falls. Carbide works in other countries sprang up where there was cheap power, as in Norway and Sweden. At first it was believed that acetylene gas, C_2H_2, which is formed by the action of water on calcium carbide, $CaC_2+2H_2O=Ca(OH)_2+C_2H_2$, had a great feature as an illuminant. Experience showed that this hope was doomed to failure; the dangerous properties of the gas, among other reasons, made its use in any but the most restricted fields, such as the lamps of motors and bicycles, and in country houses, out of the question. The invention of the oxy-acetylene blowpipe, in which acetylene is burnt with oxygen gas to produce a temperature but little below that of the electric arc, has again led to an increased use of acetylene. It has been found that the gas, which is self-explosive under pressure, so that it cannot be compressed into steel cylinders as in the case of oxygen and hydrogen, may be absorbed in acetone, a liquid solvent, soaked in a porous material such as "kapok," the seed hairs of a plant growing in India and Java. By means of the oxy-acetylene blowpipe, in which oxygen is blown into an acetylene flame, thick steel plates may be rapidly and cleanly cut and rails welded, and since the flame is produced also under water the blowpipe may be operated by divers in salvage work under the surface of the sea.

After the first slump in carbide, a new use for the material was discovered by the German chemist F. Rothe, whose work is usually credited to the technical chemists Frank and Caro. He found that when commercial carbide is heated in a current of nitrogen, the gas is absorbed, with the production of calcium cyanamide, $CaCN_2$, which serves as a fertiliser and as a source of ammonia. Pure carbide, as Moissan found, does not take up nitrogen.

The manufacture of carbide is a relatively simple operation. It presupposes a cheap and abundant source of power, so that water power is almost exclusively used. There is an experimental factory in Manchester and two small factories in Ireland, but these supply only about one-hundredth of the present relatively small consumption of carbide in this country.

There is much promise of utilising the water power of Scotland for the manufacture of carbide, but so far nothing has been done in this connection.

The electric furnaces for the manufacture of carbide are of two kinds. One type consists of a tank of resisting fireclay, lined inside with carbon, into which blocks of carbon, or electrodes, dip. The tank is filled with a crushed mixture of quicklime and carbon of relatively great purity, preferably anthracite coal. A series of electric arcs are struck between the vertical carbon electrodes and the carbon lining of the sole of the furnace, and at the high temperature developed (3,000° C.) carbide is formed in the molten condition and is tapped off periodically. The electrodes are fairly quickly consumed, and must be renewed as required.

In the second type of furnace the body of the furnace revolves, and the charge of lime and coke or anthracite is brought slowly in contact with a row of fixed electric arcs. The molten carbide formed solidifies as the furnace continues to revolve, and the material is taken away from the arcs. The continuous block of carbide formed on the periphery of the furnace is then removed.

The carbide formed has to be crushed, and this operation is somewhat dangerous, as acetylene is given off in a moist atmosphere, and may lead to explosions. The crushing is carried out in an inert atmosphere, such as nitrogen, and every precaution is taken to prevent access of moisture. The granular crushed carbide is then ready for use. It is transported in airtight packages.

The question of the economical manufacture of calcium carbide has been discussed by Mr. Charles Bingham (*J. S. C. I.*, 1918, R85). The most serious item of cost is electric power. The cost of fuel alone for electric power now exceeds 0·4d. per unit (kilowatt-hour), as compared with the total cost of power of about 0·25d. per unit under pre-war conditions. To produce 1 ton of carbide requires 4,250 units of electric energy, including the power required for accessory plant such as crushers. The cost of power per ton of carbide in this country would therefore be at least £6 13s. 4d., as compared with 22s. to 25s. in Norway, where water power is available. It is obvious that British carbide cannot, under such conditions, hope to compete with the Norwegian product. Competition would only be possible as a result of—(1) a high import duty on carbide; (2) cheaper coal; (3) the utilisation of new cheap sources of power.

The hope for cheaper coal may be estimated at its true value from the following statistics relating to the items in the cost of coal:

	Average Costs per Ton of Coal in—			
	1913.		1919.	
	s.	d.	s.	d.
Labour	6	4	19	5½
Timber and stores	1	0	3	2¼
Other costs	0	11	1	2½
Royalties	0	5½	0	6¾
Owners' profits	1	5	1	2
Compensation	—		0	3¼
Administration	—		0	2¼
Total ..	10	1½	26	0½

These prices are at the pits. The cost of carriage must be added, and it is worthy of note that the freight on anthracite to Norway is lower than the railway charges from Swansea to a carbide factory in England.

In connection with the possibility of cheaper power, Mr. Bingham is inclined to the view that the utilisation of waste gas from coke ovens and blast furnaces is the only solution. But even with gas free of charge, he points out that the working costs of gas engines amount to 0·11d. per unit under the most favourable circumstances, which amounts to £1 19s. per ton of carbide. Modern gas engines consume 27 cubic feet of coke-oven gas per kilowatt-hour, so that at 2d. per 1,000 cubic feet the gas alone would cost 19s. 2d. per ton of carbide. In any case, therefore, the plant cannot afford to pay for gas. Many large electrical generating plants are, however, owned by colliery and blast-furnace undertakings, and the load factor (the ratio of the average consumption to the maximum power generated) seldom exceeds 50 per cent., and in many cases is

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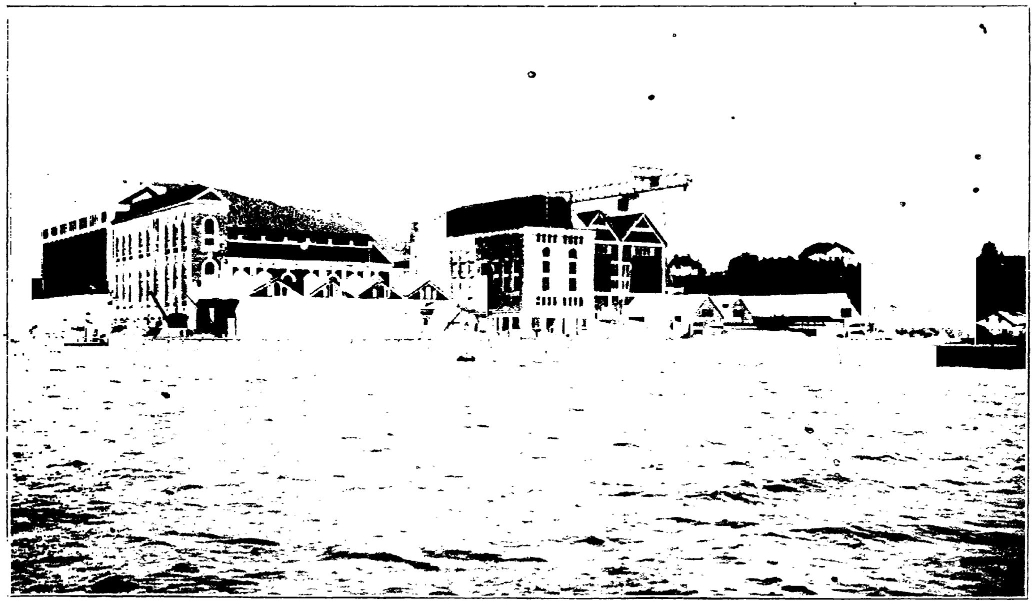
The carbide formed has to be crushed, and this operation is somewhat dangerous, as acetylene is given off in a moist atmosphere, and may lead to explosions. The crushing is carried out in an inert atmosphere, such as nitrogen, and every precaution is taken to prevent access of moisture. The granular crushed carbide is then ready for use. It is transported in airtight packages.

The question of the economical manufacture of calcium carbide has been discussed by Mr. Charles Bingham (*J. S. C. I.*, 1918, R85). The most serious item of cost is electric power. The cost of fuel alone for electric power now exceeds 0·4d. per unit (kilowatt-hour), as compared with the total cost of power of about 0·25d. per unit under pre-war conditions. To produce 1 ton of carbide requires 4,250 units of electric energy, including the power required for accessory plant such as crushers. The cost of power per ton of carbide in this country would therefore be at least £6 13s. 4d., as compared with 22s. to 25s. in Norway, where water power is available. It is burnt in blast burners. This phase of the utilisation of fue has attracted a good deal of attention in America. Powdere coal may, however, be burnt directly, in a blast of air, an the use of the fuel in this way has long been carried out successfully in America in the firing of cement kilns. The cost o grinding and of the flotation must, however, be taken int account.

The great increase in the price of coal, an increase whic shows no sign whatever of abatement, will lead to a thoroug investigation of the possibilities of utilising waste fuel, whic under the prodigal pre-war conditions had no value. It is to b regretted that steps were not taken earlier to carry out som of these investigations. Countries more fortunately situate are turning to water power. In Spain, not famous for blatan progress, there was, in 1917, 500,000 h.p. developed hydraulically, and new schemes for 15,000 and 12,000 h.p. are to b developed at Asturias and in Valencia. Further development are expected, and in time it is hoped that the country wil be independent of imported coal. The water power of th Pyrenees is rapidly being developed. About 150,000 kilowatts or about ten times the amount in 1914, is now being utilise by France. Carbide is made to the extent of 4,000 tons pe annum at Auzat, Castelet on the Ariège, and Bassens on th Garonne. It is now to be made in the State factory on th plateau of Lannemezan (50,000 h.p.), and at another a Marignac (40,000 h.p.). Nitric acid is made by the Birkeland-Eyde process at Soulom by the Norwegian Nitrogen Company When the authors visited this district in 1919 great activit was apparent.

In Switzerland a new hydro-electric station was complete near Alten-Goesgen in 1917 for 50,000 h.p. A works a Eglisau is on the point of completion, for 30,000 h.p. On at Mühlberg was to be ready in the autumn of 1920, and is t have a capacity of 32,000 h.p., and new works at Riton Barberine, and Am Steg are under construction. Extension of the existing works at Oberhalse, Rossens, La Plaine, an near Wildegg are contemplated. The power exported t Germany, France, and Italy in 1918 was 132,000 h.p., the tota output being 1·2 to 1·3 milliard kilowatts. It is believed tha

PLATE VI.



the hydro-electric developments will make the industry a seasonal one, the plants being worked for a few months in spring and summer. The cost of power will increase, so that the old price of 0·75 to 1 centime per kilowatt-hour will not be possible, but the war price of 6 centimes will be lowered.

Even at home the question of water power has taken a new interest. The chief source of water power in Great Britain is that employed by the British Aluminium Company at Kinlochleven and Foyers, where power is said to be obtained continuously at 34s. per h.p.-year. The most hopeful locality for large developments of water power (not tidal power) seems to be the Scottish Highlands.

An estimate of the world's sources of water power has recently been made as follows by Dr. Toniolo, of Milan:

Potential and Developed Hydro-Electric Power in H.P.

	Potential.	*Developed.*
United States	20,000,000	5,000,000
Canada	6,000,000	1,756,791
France	6,000,000	500,000
Norway	5,500,000	850,000
Spain	5,000,000	300,000
Italy	5,000,000	750,000
Sweden	5,000,000	600,000
Switzerland	1,500,000	400,000
Germany	1,000,000	500,000
Great Britain	700,000	60,000

This table is incomplete, since it leaves out of account very important potential sources of hydro-electric power in Iceland, Egypt, Africa, and other places, all of which may be of importance in the future. In spite of this, the figures show clearly what is possible and what has been accomplished. In the two countries Germany and Great Britain, both possessing important coal-supplies, the former has harnessed 50 per cent. of its potential water power, the latter less than 10 per cent.

The Manufacture of Cyanamide.

The manufacture of calcium cyanamide depends on bringing together calcium carbide and nitrogen gas at a fairly high temperature. The types of apparatus so far used for this purpose may be classified into three groups: (1) The Odda Method: this is used in Norway and in the United States; (2) the Oven Method, used in Germany; (3) the Continuous Process, used in Sweden.

In the Odda process the crushed carbide is packed into steel baskets, down the centre of each of which runs a rod of carbon. The charges are lowered into furnaces. The rod may be heated electrically by passing a current through it, and nitrogen gas is then passed through the closed furnace. When the reaction starts sufficient heat is given out to enable the change to be self-supporting, and the current is switched off. After some hours the absorption of nitrogen ceases, and the block of sintered material is tipped out and crushed.

In the Oven process sheet-iron containers of carbide are run on trucks into airtight iron ovens heated outside by gas, through which nitrogen is passed. The trucks of finished product are run out at one end and fresh trucks of carbide run in at the other end, so that the process is in a way continuous.

In the Continuous process a mixture of carbide, quicklime, and a flux, such as calcium fluoride, is raked mechanically over shelves in a vertical furnace, in which it is subjected to heating by a row of electric arcs. The material does not fuse in passing through the arcs, so that a porous non-sintered product is obtained. In the older continuous methods a hard fused slag was obtained.

In all cases the product is cooled, ground in an atmosphere of nitrogen to avoid explosions, and is then known as "nitrolim." It contains about 20 per cent. of fixed nitrogen as a maximum. In the new process, where lime is added to reduce the fusibility, the percentage of nitrogen is somewhat reduced.

The ground raw product is very dusty and corrosive, on account of the content of free lime and unchanged carbide. It is usually treated in some way to render it less dusty. Many processes have been proposed to attain this end.

Usually the free carbide is decomposed by mixing with a little water in a mixer, when a dry powder results, and this is then treated with oil to render it less dusty. The free lime is also hydrated in the process. Three to four per cent. of heavy tar oil is used, and the dusty character of the material is much reduced. The addition of bog-iron ore, molasses, aluminium salts, and innumerable materials, has been proposed, and the operation of rendering cyanamide non-dusty offers a splendid field to the type of inventor who has more confidence than knowledge.

The cyanamide is sent out in wooden kegs. It should be protected from atmospheric moisture, as it is rapidly impaired by water. The fixed nitrogen is then converted into forms of little utility, and the fertilising value of the material is much reduced.

The manufacture of cyanamide in Germany is in the hands of a group of firms. A total of 600,000 tons is manufactured annually. The firms making cyanamide are the following (*Note.*—" Stickstoff "=Nitrogen):

1. The Mitteldeutsche Stickstoffwerke A.G., Piesteritz (175,000 tons).
2. The Öberschlesischer Stickstoffwerke A.G., Chorzow (150,000 tons).
3. The Aktiengesellschaft für Stickstoffdünger, Knapsack and Gross-Kayna (140,000 tons).
4. The Bayerische Stickstoffwerke A.G., Trostberg and Margaretenberg (75,000 tons).
5. The Lonzawerke, Waldshut (60,000 tons).

Owing to lack of coal, attention has been directed in Germany to the development of water power, and it may confidently be expected that whatever can be done in this direction will be effected at no distant date.

In Japan, cyanamide is made in two large works, belonging to the Nippon Nitrogen Company and the Electrochemical Industry Company respectively. The production of ammonium sulphate in 1917 was 57,000 tons, and over 90,000 tons were expected in 1918. Nitric acid is to be manufactured by the arc process, and the Japanese Government has established a Central Research Station for Nitrogen Industries.

The Nippon Senryo Sieze Kabushiki Kaishi, headed by Messrs. Takimene, have acquired the rights and information of the Badische Company, as well as of the Claude process, and Dr. Tamaru spent three months at Merseburg studying all details of the latest Haber process.

During the war period nine new cyanamide works were erected in France, three by the Government, two others with Government control, and all with substantial government assistance. France has also two arc process plants (p. 207).

WORLD'S PRODUCTION OF CALCIUM CYANAMIDE.

Year.	*Quantities in Metric Tons.*	
	Calcium Cyanamide.	*Combined Nitrogen on the Basis of* 18 *per Cent. Nitrogen Content.*
1906	500	90
1907	1,700	306
1908	2,510	452
1909	11,550	2,079
1910	20,495	3,689
1911	54,506	9,811
1912	126,538	22,777
1913	181,444	32,660
1914	222,397	40,031
1915	345,133	62,124
1916	485,396	87,321
1917	668,202	120,276
1918	668,802	120,384

The parent American cyanamide works was established on Canadian soil at Niagara. It is owned by the American Cyanamid Company and produces 64,000 tons per annum. The more recent developments in connection with American Government factories will be considered later.

The first cyanamide works to be established were in Norway, and the cyanamide industry in Norway, and to a less extent that in Sweden, calls for detailed description. The production of nitrates by the arc process is also of great importance in Norway, and a table may first be given showing the total output of combined nitrogen from that country. The figures represent metric tons.

EXPORTS OF NITROGEN FROM NORWAY, 1917-1919.

	1917.	1918.	1919.
Nitric acid	1,621	8,337	—
Ammonium sulphate ..	50	—	—
Ammonium nitrate ..	63,580	49,588	5,163
Sodium nitrate	27,711	26,366	—
Sodium nitrite	3,536	2,098	—
Calcium nitrate	35,932	53,625	63,880
Cyanamide	2,313	11	9,930
Calcium carbide	46,067	41,772	25,599

The Government subsidies to the Norwegian nitrogen industry amounted to £765,000 for the period 1918-19. The effect of the Armistice on the various products is seen from the table. The consumption of home-produced nitrates in Norway is given in the following table:

1914-15	8,286 tons.
1916-17	19,490 ,,
1917-18	53,399 ,,
1918-19	49,000 ,,

The determination of Germany to regain the world's markets may be estimated from the steps she has taken in the nitrogen industry. The position is as follows: The German Imperial Economic Office and Treasury and representatives of the nitrogen industry have agreed to found a State Nitrogen Monopoly similar to the Potash Syndicate. The capitalisation of leading German chemical firms is given below in millions of marks:

	Old Stock.	*New Ordinary Stock.*	*New Preferred Stock.*	*Total Capital.*
				Million Marks.
Badische	90	90	72	252
F. Bayer	90	90	72	252
Höchst	90	90	72	252
Cassella and Company	45	45	36	126
A.G. Anilin Fabrik ..	33	33	26	92
Griesheim	25	25	20	70
Weiler-ter-Meer ..	10·4	10·4	8·32	29·12
Total capital ..				1,073·12

Early in the war the German Government appointed a trogen Administrator, with considerable powers. His first tivity was to increase the output of ammonia from gas and ke works to the maximum. The next step was to have stalled at all cyanamide plants in existence, which were rning out only cyanamide for fertilising purposes, autoclaves the production of ammonia (p. 218). Large new cyanamide rks were laid down, and for all this the Government made ry large loans. Two large cyanamide works were erected tirely from public funds.

The Haber plant at Ludwigshafen, started in 1912, was in ccessful operation just before the outbreak of war, and oduced about 7,000 tons of fixed nitrogen annually. This s developed very rapidly to 100,000 tons. This is the pau plant. The second works at Merseburg, in Saxony, s erected during the war, power being supplied from the nite fields. When this works is completed it will have a pacity of 800 tons of synthetic ammonia per day, or 1,500000, ns of synthetic ammonium sulphate per annum. Plant for s works was manufactured at Krupp's, and it embodies ny improvements (see p. 165).

During the war, therefore, the nitrogen industry in Germany s most energetically fostered by the Government, none of members of which, presumably, had any interest in Chilean rates or in shipping, or if they had, could hardly benefit them under war conditions in Germany. Control was ercised by an Imperial Commissioner for Nitrogen under War Department, who had authority to issue regulations the production and use of nitrogen products and all traffic the same. Associated with Dr. Rathenau, in charge of v materials, were Professor Caro, representing the cyanamide erests; Dr. Bueb, representing the Badische Company; d Professor Geheimrat Bruckner, representing the by-oduct industry. The fact that these posts were filled by entific men must appear strange to British Government cles.

Even before the end of the war, Germany began to consider future interests in the commercial aspects of the nitrogen lustry. In August, 1918, the association of producers, the

Stickstoffsyndicat, referred to on p. 197, was formed, largely established under Government influence, the capital stock of which is held conjointly by the Badische Company, the cyanamide group, and the affiliated coke-oven and gasworks companies. Each of these interests nominates one director, the fourth member of the board being a Government representative. A further board of managers, whose chairman is nominated by the Government, looks after the business side of the concern. The syndicate determines from time to time what is to be the production of each group. It allotted, in 1919, 300,000 tons of nitrogen to synthetic ammonia, 93,000 tons to cyanamide, and 120,000 tons to by-product industry, fixing the ultimate prices in accordance with the relative fertilising values of the products (see p. 32). All the output of fixed nitrogen was to be pooled; export was to be allowed only after home requirements had been met. With a view to safeguarding other interests, Germany also set up a body consisting of twenty-two members representing producers and consumers of nitrogen products, called the Nitrogen Commission. The Government, the Stickstoffsyndicat, and the agricultural interests, have five members each. The fertiliser manufacturers, fertiliser dealers, the German Board of Trade, and the German Board of Agriculture, together with some other interests, have one member each. This is a formidable organisation.

Power Used in Nitrogen Fixation.

The power used for nitrogen fixation is shown in the table below, taken from the Statistical Supplement to the N.P.C. Report. This table shows only the two main processes in which power is a primary factor. The installed capacity of the power plants employed for nitrogen fixation in 1920 amounted to over a million kilowatts when allowance is made for the reserves always provided. The actual number of kilowatt-hours required to produce the full output of the arc and cyanamide plants in 1920 was nearly double the combined actual output of the whole of the electricity stations of the British Islands, including lighting, power, and traction.

WORLD'S CONSUMPTION OF POWER IN NITROGEN FIXATION.

Process.	1913.		1920.	
	Installed Capacity in Tons Nitrogen.	*Actual Power required in Continuous Kilowatts.*	*Installed Capacity in Tons Nitrogen.*	*Actual Power required in Continuous Kilowatts.*
Cyanamide	59,500	130,000	325,500	715,000
Arc..	16,900	142,000	33,300	316,000

Prices of Nitrogen Fertilisers in Germany.

The table below shows the price of nitrogen fertilisers in Germany in 1919 (from Statistical Supplement to N.P.C. Report), at which time the output from each industry and the prices were controlled by the Government. The tax was imposed and graduated so as to bring the price per ton of nitrogen sold as fertiliser to a total figure for each of the three products—cyanamide, ammonium sulphate, and sodium nitrate (all synthetic)—in the ratio of 8, 9, and 10 respectively, since this ratio is stated to represent the approximate relative fertilising value of the nitrogen in the three forms.

Per Metric Ton Nitrogen as—	*Price in Marks in 1919.*			
	At Works.	*Direct Tax.*	*Total to Industry.*	*Ratio of Totals.*
Cyanamide	1,400	3,450	4,850	8
Ammonium sulphate ..	2,900	2,500	5,400	9
Sodium nitrate	3,400	2,600	6,000	10

These must be regarded as an index of home prices only. Late in 1919 the exchange rate with England varied from 100 to nearly 200 marks per pound sterling, and if 150 marks is assumed, the following very low prices would be obtained:

Price per Metric Ton of Nitrogen as—	*At German Works.*	*To Fertiliser Industry.*
	£	£
Cyanamide	9·3	32·3
Ammonium sulphate ..	19·3	36·0
Sodium nitrate	22·7	40·0

At the present time (April, 1921) the rate of exchange has for some time been 240 marks to the pound sterling, and, assuming this figure, we obtain the following prices:

Price per Metric Ton Nitrogen as—	*At German Works.*	*To Fertiliser Industry.*
	£	£
Cyanamide	14·9	51·5
Ammonium sulphate ..	31·0	57·6
Sodium nitrate	36·3	64·0

The present prices per metric ton of fixed nitrogen in the forms in which it is available in the United Kingdom—viz., Chile nitre and recovery ammonium sulphate—are (1921):

Sodium nitrate from Chile	£140.
Ammonium sulphate	£122 15s.

If the rate of exchange with the mark were normal, the selling prices of the German products would be:

	At Works.	*To Fertiliser Industry.*
	£	£
As cyanamide	70	242·5
As ammonium sulphate ..	145	270
As sodium nitrate	170	300·0

There is no doubt that great changes in economic conditions have taken place in Germany since 1919. Wages, which were approximately three times the pre-war level in 1919, are now (January, 1921) six to eight times. If the figures for the selling prices in 1919 are taken to include a 10 per cent. profit, the German costs of production per metric ton of fixed nitrogen in marks would be:

As cyanamide	1,260.
As ammonium sulphate	2,610.
As sodium nitrate	3,060.

Assuming that the ratio of wages paid governs roughly the cost of production, the pre-war costs of production in Germany of the above products would be 420, 870, and 1,020 marks respectively, or £21, £43·5, and £51, on the basis of pre-war exchange. These figures may be compared with the estimates made by the Nitrogen Products Committee and included in other parts of the present volume: £24, £29, and £51. The first and third agree, but the cost of production of synthetic ammonium sulphate by the Haber process had been fixed at much too low a figure. The prices of nitrogenous fertilisers in Germany in December, 1921, were as follows, in marks per kilogramme of fixed nitrogen: Ammonium sulphate (technical quality), 25·80; ammonium sulphate (dry and acid-free), 26·40; sodium nitrate, 31·2; cynamide, 23. The prices for British ammonium sulphate for 1922 are announced as follows: Neutral quality per ton—January, £16 3s.; February, £16 13s.; March to May, £17 3s. The corresponding prices for ordinary quality are £15, £15 10s., and £16. Sodium nitrate was £14 per ton in January.

At the time of writing (April, 1921) it is announced in the technical press that the German Nitrogen Syndicate (see p. 197) had made a "remarkable proposal" to the British Sulphate of Ammonia Federation. The effect of this is that the Federation and other groups of British nitrogen producers and distributors should pay to Germany a large sum of money in cash, in consideration for which Germany would agree greatly to reduce her exports of nitrogen for next session. This proposal, it was stated, had been unanimously rejected. It is evident, however, that something more than this will have to be done. The facts which have so long been known to scientific men in this country will gradually become clear even to the business man. It would be expected that Germany's offer might help in this work of education. In the Annual Report of the British Sulphate of Ammonia Federation issued later in 1921 it was announced that a working agreement had been made between the four chief nitrogen-producing countries at Rotterdam, but no details are given.

Nitrogen Fixation in France.

In France the production of synthetic nitrogen compounds in 1920 was at the rate of 250,000 tons per annum, and when the extensions of the works are completed the capacity for production will be 400,000 to 500,000 tons per annum. The production of cyanamide in France has increased from 75,000 to 200,000 tons per annum.

The official policy in France before the war was to lay in stocks of explosives sufficient, in the judgment of the military authorities, to last out a "short, sharp war." The phenol required was obtained from Germany. In the middle of September, 1914, the use of explosives by the artillery was exceeding very considerably the amount estimated by the military authorities, and it was necessary to provide daily 40,000 to 50,000 75-mm. cartridges and to make schneiderite and ammonium perchlorate for trench mortars. The need for explosives continually increased, and it became evident that the character of the war was not at all like that for which the country had been prepared. A great national effort was required, and the part which the chemists of France played in this can be appreciated from the following table, giving the requirements of the army in metric tons per day:

	Propellants.	*Nitrogenous Explosives.*	*Chlorate and Perchlorate Explosives.*
Mobilisation	24	0*	0*
January 2, 1915	80	100	—
June 6, 1915	104-135	125-195	—
October 19, 1915	238-313	351-654	109-135
December 25, 1916	441-550	728-936	150-159
June 25, 1917	484-640	859-940	148-124
February 28, 1918	444	625	—

After April, 1918, the requisitions for explosives amounted to about 390 tons per day.

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* Provided in stocks accumulated.

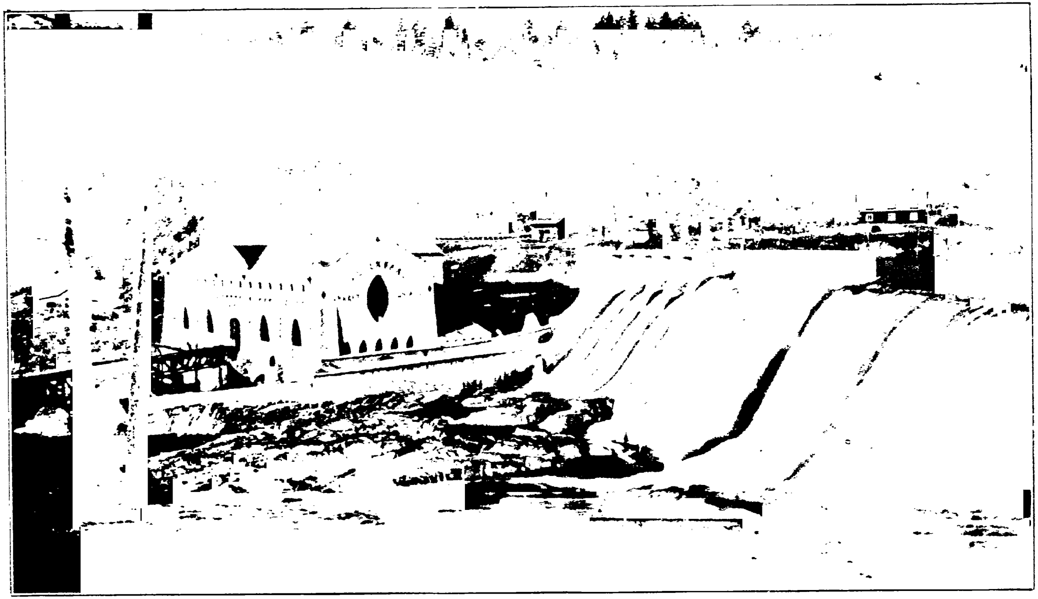
Before the war there were eighty-seven scattered works for the manufacture of sulphuric acid, producing 13,500,000 tons of 53° Bé acid, of which 975,000 tons were used for the manufacture of superphosphates and the rest concentrated to 68° acid. This output was reduced by 15 to 20 per cent. by enemy occupation of territory. The production of explosives called for large quantities of concentrated acid, and steps were taken to force the production of the chambers from 5 to 6 kilogrammes of acid per cubic metre to 7 to 8 kilogrammes, and to increase the Kessler and Gaillard concentrating plant in the ratio of 1 to 20. The use of acid was also restricted in industry, and nitre cake began to be used in August, 1915. The Volvic lava of Puy-de-Dôme proved invaluable in the construction of concentrating apparatus. In addition, there were needed for the transport of acid 2,000 20-ton tank wagons, 600 platforms for which were made in England and Spain.

Oleum containing 20 per cent. sulphur trioxide was exclusively used, the consumption amounting to 1·5 to 1·9 tons per ton nitrocellulose, and 2·2 tons per ton of trinitrotoluene. The oleum was, at the outbreak of war, made in a few works only, one of which at Thann (Alsace) came under fire in 1914 and was transported by night to Saint-Denis, where it was re-erected and came into operation in 1916. All the common processes (Tentelew, Grillo, and Mannheim included) were used, and a monthly output of 21,000 to 22,000 tons was secured. New works were put in hand, and in the meantime oleum was imported from America. The monthly consumption of sulphuric acid and oleum was as follows, in metric tons:

	66° *Bé Acid.*	20 *per Cent. Oleum.*
February, 1915	6,000	1,000
January, 1916	42,000	5,000
January, 1917	80,000	20,000
January, 1918	60,000	19,000
June, 1918	40,000	18,000

Nitric acid was produced before the war almost exclusively from Chile nitre by the retort process, and during the war

PLATE VII.



LIENFOS POWER STATION.

great extensions of these plants were made. The stock of nitre at the end of 1915 amounted to 90,000 tons; it increased during 1916, but from the beginning of 1917, when the submarine campaign was begun, the stocks of nitre diminished. In 1917 numerous ships laden with nitre were torpedoed. On account of the large amounts of raw material (coal, pyrites, and nitre) required in the manufacture of explosives, necessitating great shipping demands, it was decided in 1917 to ask the American Government to supply explosives ready made. A programme was agreed upon, but the actual deliveries from America fell far short of the promises. Help was also given by Great Britain. The consumption of nitre and nitric acid (calculated as sodium nitrate) in metric tons per month was as follows:

January, 1915 ..	.. 3,600	March, 1916 ..	.. 25,000
August, 1915 ..	.. 9,600	July, 1917 ..	.. 42,000

On account of the transport and storage difficulties, it was decided to produce nitric acid by synthetic methods. These had an additional advantage—*i.e.*, the economy in sulphuric acid which would otherwise be required in decomposing the nitre, which was even more important than the nitric acid. Before the war synthetic nitric acid was made by the Pauling arc process at La Roche-de-Rame, at the rate of 2 tons of 50 per cent. acid per day. This was continued, but a new factory on the Birkeland-Eyde principle was erected by the Société Norvégienne de l'Azote at Soulom, utilising 12,000 kilowatts from the hydro-electric installation in the Hautes-Pyrénées of the Compagnie des Chemins de Fer du Midi. This works delivered 300 tons of nitric acid a month, partly as nitrates. The ammonia-oxidation process was also largely used, the ammonia being derived from cyanamide. The first works was installed at the Poudrière Nationale d'Angoulême. Carbide was imported from Switzerland and converted into cyanamide by the Société des Produits Azotes, nitrogen being obtained by the Claude process at Martigny, Notre-Dame de Briançon, and especially Bellegarde. From 2,650 to 3,500 tons of cyanamide per month were delivered at Angoulême. The first oxidation plants were operating in the autumn of 1916, and the whole were in operation in 1917. The programme was much enlarged in 1917 on account of the submarine warfare, and it was then decided to erect factories for making 500 tons of nitric acid and 150 tons of ammonium nitrate per day by the oxidation of ammonia. This programme required 800 tons of calcium carbide per day and 125,000 kilowatts. Water power of the Pyrenees, Central France, and the Alps, and even central steam-power plants at Nanterre and Carmaux, were brought into requisition. The most important works was at Lannemezan (50,000 kilowatts), and new oxidation works were installed at Toulouse, Bassens, Sorgues, and Saint-Chamas. Toulouse and Bassens had begun to operate at the Armistice; the others were nearly finished. These works would have supplied all requirements in nitric acid and ammonium nitrate.

The American effort is formidable. The new Government plant at Muscle Shoals is capable of producing 250 tons of nitric acid per day from cyanamide. The over-all efficiency from cyanamide to acid is 87 per cent., that from ammonia to acid practically 90 per cent. The cost of the works was 75 million dollars. In 1919 it was decided to set up a civilian organisation known as the United States Fixed Nitrogen Administration, under the joint control of the Secretaries of War, Navy, Interior, and Agriculture.

Italy has five cyanamide plants and two arc process plants, with a total capacity of about 20,000 tons of nitrogen annually. While the industrial situation since the war has prevented very definite developments, it is understood (*cf.* p. 182) that very close relations have been established with the Germans as to future commercial nitrogen developments, and it is regarded by experts as certain that large-scale fixation plants will be put down in Italy within a very short period.

'Austria was one of the pioneers in both the cyanamide and arc processes. There are no definite statistics as to the extent of war developments, but this country possesses at present two cyanamide plants with a capacity of 22,000 tons of nitrogen and some older small arc plants (see p. 237).

In Norway there is a large cyanamide plant, at Odda, owned by a British company, the Alby Carbide Company. In Sweden there are two completed cyanamide plants; the erection of a third, with the accompanying large power development, was commenced during the war, but was interrupted by the bursting of a partly erected dam by flood.

In Switzerland there are three cyanamide works and two small arc plants using the new process (p. 253).

Although the Nitrogen Products Committee strongly recommended the erection of cyanamide works in Great Britain during the war, nothing was done (p. 187), and this country is still—almost alone among the civilised nations of the world—without any nitrogen-fixation industry.

The view which was often expressed during the war period, and is still apparently held in some quarters, that the cyanamide process is a thing of the past in comparison with the synthetic ammonia process, is directly falsified by the above figures. There can hardly be any doubt that the original recommendation of the Nitrogen Products Committee in 1919 that the war requirements of this country could most certainly be met within a reasonable period by the manufacture of cyanamide was entirely just.

The Manufacture of Cyanamide at the A.G. für Stickstoff-dünger, Knapsack, Germany.

This factory is situated in the brown coal fields a few miles south-west of Cologne, and is engaged in the manufacture of calcium carbide, cyanamide, urea, and synthetic acetic acid. It is understood to have affiliations with the Griesheim Elektron and to dispose of their synthetic acid to Meister Lucius and Brüning, and also to the Bayer Company at Leverkusen.

As it now stands the plant cost some 30,000,000 marks, which represents, in part, a 15,000-h.p. power plant, a carbide plant with a capacity of 8,000 tons per month, a cyanamide plant of 11,000 tons per month, the acetic acid plant for 450 tons per month, the ammonia oxidation, urea, and gas-producer plants. When working at full capacity they employ about 2,000 men.

Cyanamide Process in General.—The process may be considered in five steps—

(1) The manufacture of calcium carbide.
(2) The crushing of the carbide.
(3) The liquefaction of air to obtain nitrogen.
(4) The manufacture of the cyanamide proper.
(5) The crushing of the cyanamide.

1. **Manufacture of Calcium Carbide.**—The raw materials used and the quantities of finished products turned out by the plant are as follows:

Raw Material.	*Present* Stock (Tons).*	*Consumption in Tons per Month.*		*Source of Supply.*
		Present.	*Full.*	
Burnt lime	1,600	2,400	8,000	50 per cent. from occupied territory.
Coke	8,000	900	3,000	Ruhr.
Anthracite, "Margerusskohle IV."	5,000	900	3,000	Unoccupied territory.
Electrodes	400	120	400	Duisberg and Berlin.
Calcium chloride ..	200	150	500	Chem. Fab. Kalk.

Finished Products.	*Present Stock (Tons).*	*Consumption in Tons per Month.*		*Destination* (1918).
		Present.	*Full.*	
Calcium carbide ..	100	3,100	8,000	2,100 tons to cyanamide, rest to occupied territory at present.
Cyanamide ..	900	2,600	10,000 11,000	All to occupied territory at present.
Acetic acid ..	—	—	450	Process worked for Meister, Lucius, and Brüning, of Höchst.
Fuel:				
Raw brown coal..	—	75,000	140,000	
Briquettes for heating, etc. ..	—	3,000	3,000	

* This refers to June, 1919.

It is understood that there are in all ten carbide furnaces—six of 30 tons, per twenty-four hours capacity, three of 25 tons, and one of 45 tons. The first six are of rectangular form with dimensions of approximately 12 feet by 8 feet by 5 feet, and divided off into three compartments by means of partitions of firebrick. A system of two electrodes is in use, the bottom of the furnace, which is lined with graphite, being one, and the other consisting of three vertical carbons, or one carbon per compartment. These carbons are built up of three blocks some 5 to 6 feet in length, and having a cross-section of about 18 inches. They hang suspended from an overhead trolley, and are cooled by the customary water-jacketed equipment. They are gradually lowered into the furnace until all but 18 inches of the electrode has been consumed, at which point they are renewed.

Transformers situated near the furnaces receive the current at 800 to 1,000 ampères and 6,000 volts, and transform it to 33,000 ampères at 133 to 166 volts. This gives a current density at the electrodes of approximately 5 ampères/cm.^{2}.

The burned lime and anthracite are brought in on an overhead trolley to a platform at the level of the top of the furnace, and are there mixed by hand in the proportions of 100 parts lime and 66 parts anthracite.

The charge is thrown on continuously by hand, but the furnace is only tapped every hour. For this an auxiliary electrode is used to pierce the side of the furnace, and the operation carried out in the usual manner. The hot carbide is poured into small cars running on tracks and equipped with suitable means for dumping the cooled carbide cake. The cars are flat-bottomed and only about 8 inches deep, giving a cake of the proper size for the jaw crushers, which need not be broken up by hand.

2. **Crushing of the Carbide.**—With the "water test" the finished material gives 230 to 270 litres of acetylene per kilogramme of powdered carbide. The requisite fineness is arrived at by crushing in three stages—(*a*) Jaw crusher giving 2-inch pieces; (*b*) jaw crusher giving nut size; (*c*) tube mills giving the powdered material. The cooled carbide is thrown into a large-size jaw crusher driven by a 300-h.p. A.C. motor, and

the 2-inch size lumps here obtained are carried on an endless bucket-conveyer up to a platform some 30 to 35 feet overhead and there fed into four smaller jaw crushers. In the latter instance much fine carbide dust, otherwise lost into the air, is collected by means of settlers, of which there are two for the four crushers, each settler being connected to two crushers. The fine dust is then used directly for cyanamide manufacture. This dust represents only a small portion of total crushed product, but is nevertheless an appreciable amount and not to be neglected.

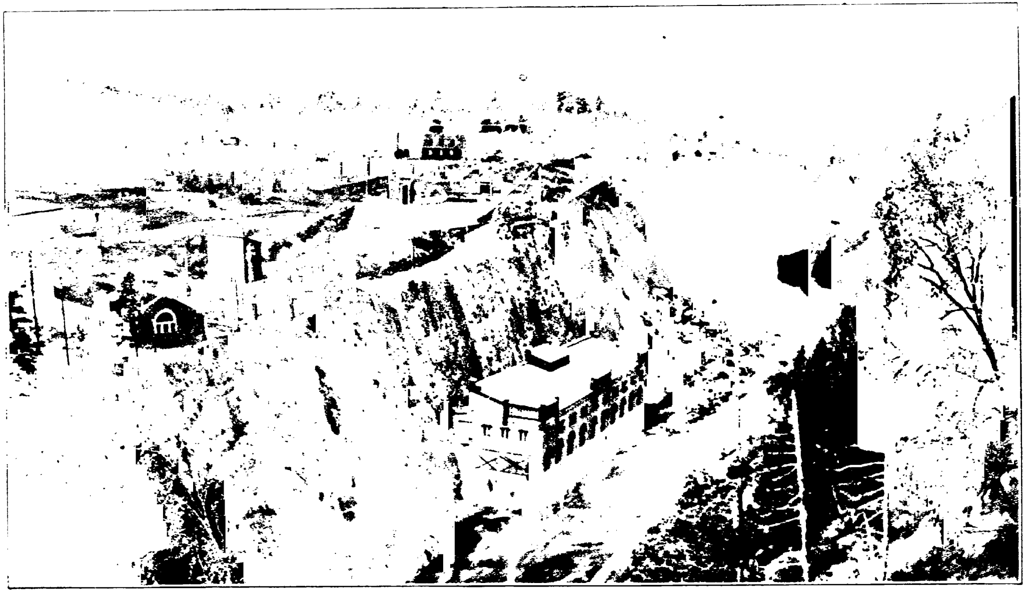
The main part of the carbide is reduced in the four jaw crushers to nut size and falls down through chutes into hoppers, from which it is fed into six tube mills. Here it is mixed with calcium chloride to the extent of 10 per cent. of the total mass. This reduces the temperature required for the absorption of nitrogen.

The tube mills are divided off into compartments, in each of which are steel rods of about 1½ inches diameter and 5 to 6 feet long. Considerable trouble is experienced with the dust.

3. **The Liquefaction of the Air to Obtain Nitrogen.**—Nitrogen is prepared by the Linde process, the liquid-air plant consisting of three sets of compressing apparatus, each of 1,800 $m.^3$/hr. capacity. Two are kept in operation and the third serves as a stand-by—a most necessary point, as nitrogen is not stored, but prepared as needed, and fed direct to the cyanamide furnaces. The air is drawn from a distance of about 1 kilometre to avoid any possible contamination from acetylene, which permeates the whole factory when the plant is operating.

4. **The Manufacture of the Cyanamide Proper.**—The mixture of 90 per cent. powdered carbide and 10 per cent. calcium chloride is carried overhead in a closed belt conveyer to the cyanamide plant, and is there fed from hoppers into the cyanamide cans. These are of rectangular shape with dimensions of approximately 1½ feet by 1 foot by ¾ foot, and consist of a sheet of thin iron and a perforated bottom which may be removed when the cans are to be emptied. The bottom and sides are covered with paper when the carbide is run in, and a piece of cardboard laid on top when the can is full, the paper burning off when the cans are introduced into the furnace.

PLATE VIII.



SVAELGFOS POWER STATION.

To face p. [illegible]12.

Fifteen of these cans are piled on a small car, which runs on a track into the entire length of the furnaces.

The furnaces, of which there are sixteen, are about 120 feet long and 6 feet in diameter, of 2-inch iron, with the track for the cars running along the full length of the bottom. For some 80 to 90 feet of their length they are set in fire-brick, to allow of indirect heating by gas produced from lignite. The nitrogen is fed in from one end and the carbide trucks run in at the other, heated, end. Every eight hours three cars are pushed into a furnace with an electric ram operating on a small electrically driven truck which runs on a track the entire length of the room. At the end of twenty-four hours three trucks or forty-five cans of cyanamide have reached the nitrogen end of the furnace, and are pushed out and allowed to cool. The cooled material is then ground in the same manner as was the carbide, and is ready for packing and shipment.

The finished material contains an average of from 16 to 22 per cent. nitrogen, and 0·75 per cent. calcium carbide. Much carbide is converted into lime in the nitrogen furnaces, since the door at the nitrogen end of the furnace must inevitably admit a large amount of air during charging. At the heated end of the furnace less air enters, as a steady stream of nitrogen (about three times the theoretical amount) passes through the furnace.*

The Largest Cyanamide Factory in the World.

We shall conclude this account of the technical manufacture of cyanamide by a description of the largest works designed for this process in the world—namely, the American factory at Muscle Shoals, Alabama, which was erected by the United States Government during the war for the purpose of supplying nitrates for the manufacture of munitions. Although this works cannot compare as a feat of chemical engineering with the German synthetic ammonia factories at Oppau and Merseburg, described in the last chapter, yet it represents a magnificent effort under war conditions, and is of the very greatest interest in the study of nitrogen-fixation processes (A. M. Fairlie, *Met. and Chem. Eng.*, 1919, **20**, 8; C. Jones, *ibid.*, 1920, **22**, 417). Cyanamide had been made since 1909 at Niagara, and at the outbreak of war this plant had a capacity of 64,000 tons per annum. Late in 1917 the American Cyanamid Company formed a subsidiary company, the Air Nitrates Corporation, to erect the U.S. Nitrate Plant No. 2 at Muscle Shoals, Alabama, for a capacity of 110,000 tons of ammonium nitrate per annum. Plants 3 and 4 at Toledo and Cincinnati, respectively, were completed as buildings only at the time of the Armistice.

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* The authors are indebted to Dr. E. C. Worden, of New York, for the material used in this account of the Knapsack works, which he visited in June, 1919. *Cf.* Allmand and Williams, *J. S. C. I.*, 1919, **38**, 304R.

In the construction of Plant 2 at Muscle Shoals 20,000 men were employed on a site of 2,200 acres, a town of 12,000 people coming into being. Muscle Shoals is on the Tennessee River, between Sheffield and Florence. The parts of the plant comprise—(1) the Power Plant; (2) the Carbide Materials Department; (3) the Carbide Furnaces Department; (4) the Carbide Mill Department; (5) the Nitrogen Department; (6) the Cyanamide Department; (7) the Cyanamide Mills; (8) the Ammonia Gas Department; (9) the Nitric Acid Department; (10) the Ammonium Nitrate Department. All these are laid out in order from north to south, except the nitrogen plant, which is placed far to the east to avoid contamination of the air used with gases from the other parts of the plant.

The power plant will ultimately be hydro-electric (*Chem. and Met. Eng.*, 1920, **22**, 417). The present scheme of 90,000 kilowatts is partly generated by a steam-power plant of 60,000 kilowatts at the works and partly supplied (30,000 kilowatts) by the Alabama Power Company from a steam plant at the Government-owned extension of the Warrior River power plant on the Alabama coalfields at Gorgas, and transmitted eighty-eight miles. At Muscle Shoals Westinghouse turbines and generators, 60-cycle, 3-phase, 12,200 volts, are used, the power being transmitted through a brick and concrete bus tunnel 8 feet high, 22 feet 10 inches wide, and 3,600 feet long. The erection of a dam at Muscle Shoals for hydroelectric power is now proceeding, and completion is expected in 1922 at a cost of over £4,000,000. The works itself cost £20,000,000.

The Carbide Section.—Limestone crushed to ½ inch to 2 inches from Government quarries twenty miles distant is discharged from cars at the north end of the limekiln building by dumping from drop-bottom cars or with a crane. It is carried by a conveyer belt to a bucket elevator, hoisted to the upper floor, and distributed by a conveyer belt among seven concrete silos, each of 6,000 cubic feet capacity. The stone is fed to the kilns by a cradle feeding device. There are seven rotary kilns, 8 feet diameter and 125 feet long, nearly horizontal (5 feet in 125 feet) steel shells lined with firebrick and rotated at ½ r.p.m. by bevel gears. The stone is fed into the upper end and fired at the lower end by powdered coal and air blast. The temperature reaches 760 to 1,090° C., and the process is continuous, three to four hours being required. The capacity of each kiln is 200 tons raw stone per day. The quicklime is discharged into seven horizontal cooling kilns, 5 feet diameter and 50 feet long, turning 3 r.p.m. The cooled lime is then sent to the raw materials building.

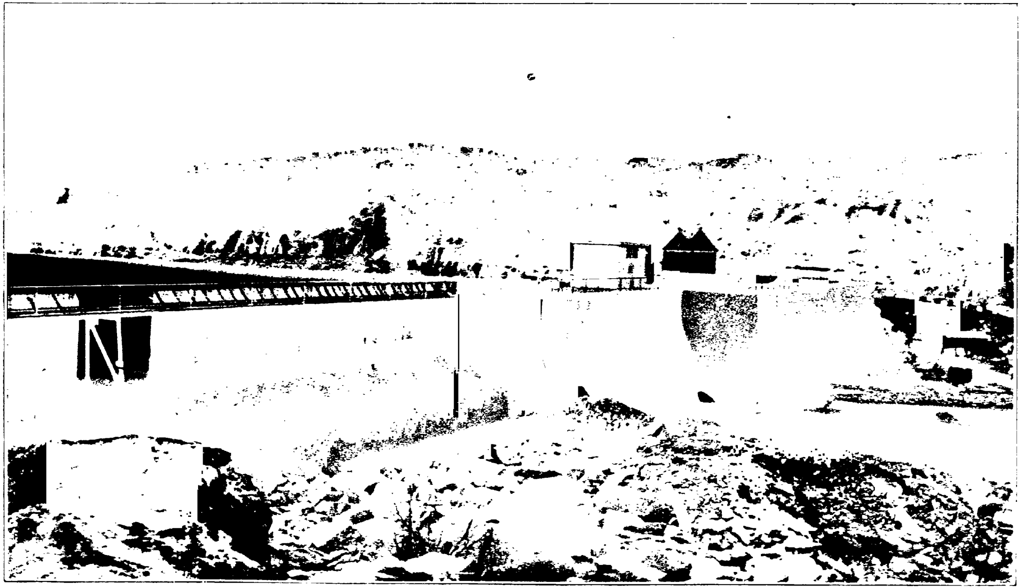
The coal-mill building, situated alongside, comprises a bin, crusher, silo, and drier. The dried coal is fed to four Fuller pulverising mills, and is elevated to steel silos opposite each limekiln, from which it is fed by the air blasts.

In the coke-drier building the coke is crushed, screened, and dried in coal-fired rotary driers. It is then conveyed to eight silos in the raw materials building for use in the carbide furnaces. In this building the coke and quicklime are weighed by two Schaffer poidometers beneath the two bins, operating continuously and set to weigh out exactly the right amounts of coke and lime, which are then delivered to a conveyer belt and transferred to the carbide room. The mixed charge is distributed to twenty-four steel silos in the furnace house.

There are twelve rectangular carbide furnaces, two spare, each 12 feet by 22 feet by 6 feet inside, composed of steel boxes open at the top and lined with firebrick. The electrodes are assembled in a separate room, and are 16 inches square and 6 feet 5 inches long. A copperhead is bolted on one end, three electrodes are fastened together as a unit, covered with wire netting and pasted with asbestos and retort cement, afterwards baked in an electric furnace. Each assembled electrode weighs 7,000 pounds. The heads are water-cooled. Three complete assembled electrodes are suspended over the top of the furnace. The depth of immersion is controlled automatically at the switchboard. The bus bars are $\frac{5}{16}$ inch thick and 8 inches wide, and there are sixteen bars to each electrode. The voltage for the carbide furnaces is 130, stepped down from 12,000 by transformers. There is one bank of transformers per furnace, each of 8,325 kilowatts. The current is 20,000 ampères, the normal capacity of a furnace is 48 to 50 tons of carbide per day of twenty-four hours. The temperature is 3,000° C., the power consumption 124 kilowatt-days per ton of 80 per cent. carbide, the electrode consumption 50 to 70 pounds per ton of carbide. Carbon monoxide burns at the top of the furnaces. At the bottom of the furnace is one layer of graphite electrodes, 16 inches square and 48 inches long, and a layer of tar and gravel on the top. In starting a layer of coke is thrown in, then a charge of 1,000 parts of lime to 600 to 620 parts of coke, previously mixed as described. This is shovelled from the floor until the furnace is full. The first tap of carbide is made six hours from starting, and then the furnace is tapped every forty-five minutes, the charge being renewed the whole time. The furnace is tapped by burning out the tapping hole with a portable electrode, and the molten carbide flows into chill cars of ½ ton capacity. After tapping, the hole is stopped by throwing a few shovelfuls of powdered carbide at the outlet, when the outflowing mass soon solidifies. The chill cars are hauled by electric locomotives to the carbide cooling house.

In the carbide mills the carbide pigs are picked off the cars by cranes and set aside. Considerable shrinkage occurs, and the blocks, when sufficiently cool, are dumped on to the crusher platform.

There are three crushers reducing to 1¼ inches, and three mills (one spare) grinding to pass 80 per cent. through 40-mesh screen and the rest through 10-mesh screen. There are then three tube mills pulverising so that 85 per cent. will pass through 200-mesh screen. Each unit deals with 15 tons per hour. All these operations are done in an atmosphere of nitrogen to prevent explosions. The milled carbide is conveyed to eight silos in the cyanamide building.



DAM OF LAKE MOESVAND.

[illegible]

The Nitrogen Plant.—The intakes are two 36-inch pipes extending north and south from the building. The air is drawn in by Root cycloidal blowers and sent through sixteen scrubbing towers, 8 feet diameter and 30 feet high, packed with 6-inch spiral rings and fed with 17° Bé caustic soda to remove carbon dioxide.

The nitrogen plant is of the Claude system. There are fifteen compressor units furnishing air at 600 pounds pressure to thirty nitrogen columns. The compression is done in three stages—30 pounds, 140 pounds, and 600 pounds. Six columns are spare. The columns are oval in shape, 4½ feet diameter and 24 feet high. The rectifier consists of a series of superposed horizontal trays, each 1½ inches deep, with a layer of liquid resting on it. The compressed air expands from 600 pounds to 50 pounds, operating a small engine giving 4 to 5 h.p. to waste, and enters the rectifier below the critical temperature. A small part of the air at 600 pounds is admitted, and the pressure liquefies the air. The liquid, containing 45 to 50 per cent. of oxygen, goes to the bottom of the column, and after spraying with liquid nitrogen the gas escaping at the top is 99·9 per cent. nitrogen. This gas is passed through two heat exchangers to a 30-inch main to the cyanamide building. It escapes from the rectifier under a pressure of 10 inches of water and goes to the building at 4 inches. Each column produces 500 cubic metres of nitrogen per pour. (The largest Linde machine produces 1,000 cubic metres.) The oxygen is allowed to escape to waste (see p. 12).

The Cyanamide Furnace Department.—There are 16 rows of furnaces, 96 in each row, or 1,536 in all. Of these, 1,500 are in operation. These rows are in two sets, one on each side of a central gangway in the building. In this gangway the paper liners are made. The furnaces are 4 feet 4 inches outside diameter, and 2 feet 10 inches inside diameter, and 5 feet 4 inches deep. They are steel shells with 9 inches firebrick lining. To charge a furnace a cylindrical paper tube container 2 feet 6 inches diameter, with a vertical paper tube 3 inches diameter in the centre, is inserted into the cold furnace and a charge of 1,600 pounds of milled carbide put in. There is an annular space of 2 inches between the paper and furnace wall. The carbon electrode is a ⅝-inch pencil, 6 feet 6 inches long, inserted in the paper tube. The covers are put on and the outer cover luted with sand.

The nitrogen is brought in by an 8-inch pipe between each pair of furnaces, and two 1½-inch pipes carry off to the furnace, one to the bottom at the centre and the other at the side 6 inches above the bottom, each provided with a valve. The nitrogen reaches the furnace under a pressure of 3 to 4 inches of water.

Single-phase currents of 100 volts and 200 to 250 ampères is turned on through the carbon rod for twenty minutes, and is then cut down to 50 volts and 100 to 115 ampères for twelve hours. The reaction gives out heat, and is allowed to continue without current for twenty-eight hours altogether. The temperature in the furnace is about 1,100° C.; the material does not melt, but sinters into a solid cake. The product contains about 63 per cent. $CaCN_2$, 2 per cent. CaC_2, 13 per cent. CaO, and 11 per cent. C. The finished material is conveyed to a mill which is an exact duplicate of the carbide mill. It is pulverised so that 95 per cent. passes 200 mesh, all in an atmosphere of nitrogen. The milled material is fed at a controlled rate to the hydrating troughs, of which there are three, 36 feet long and 3 feet diameter, each containing a horizontal shaft with projecting arms 20 inches long. Water is sprayed in at the feed end at a calculated rate to decompose the unchanged carbide. The material at the exit must be perfectly dry. The agitator rotates at 50 r.p.m., and conveys the material at the rate of 50 feet per minute. The cyanamide is conveyed through an overhead tunnel to the ammonia autoclave building, 300 feet away.

The Ammonia Autoclave Building.—This contains fifty-six autoclaves in seven units, one spare, rated at 100 tons per unit per day. They are of 1¼ inch steel and cylindrical, 8 feet diameter and 20 feet high, each provided with a vertical agitator revolving twelve times per minute. A 2 per cent. solution of caustic soda is run in to a depth of 9 feet, and 300 pounds of soda ash added, which reacts with the 13 per cent. of free lime in the cyanamide to form caustic soda of about 3 per cent. strength. The charge of 8,000 pounds of cyanamide is added from weigh bins. The acetylene from the 2 per cent. still undecomposed carbide is allowed to escape through one valve through an exhaust fan. The outlet pipe is then tightly closed and steam from special boilers admitted at 150 pounds for twenty minutes. Ammonia forms, the reaction being exothermic. When the pressure reaches 250 pounds, the ammonia valve is opened cautiously, but the pressure is maintained for three hours, The pressure then falls and the ammonia is allowed to escape. The valve is shut again, and steam admitted a second time for twenty minutes. The reaction proceeds at 200 pounds pressure for one and a half hours. The escaping gas contains 25 per cent. ammonia and 75 per cent. steam. It passes through a header and seven mud drums, followed by seven ammonia column stills, each 10 feet diameter and 25 feet high, containing sixteen horizontal plates. The gas enters at the bottom and bubbles through caps over 4-inch holes in the plates, passing to fourteen condensers arranged in seven sets of two in series, containing vertical tubes through which water circulates and steam is condensed. The ammonia gas passes through a 28-inch pipe, tapped by two 20-inch mains, one conveying 55 per cent. of the ammonia to two 60,000 cubic feet gasholders for the ammonia-oxidation plant, and the other 45 per cent. to the neutralisation plant for ammonium nitrate. The capacity of the plant is 1,000 tons of ammonia gas per week.

The autoclave sludge is blown out through an 8-inch outlet at the bottom by means of steam or air and falls by gravity to twenty rotary filters, five spare, operating under 20-inch mercury suction, where the 2 per cent. caustic soda solution is drawn off and returned to the autoclaves.

The hydro-electric development at Muscle Shoals comprises a dam, the "Wilson Dam," which it is estimated will cost $20,000,000. This dam, in course of erection, has a spillway crest of 3,080 feet, a height of 94 feet, and a total base of 177 feet. Fifty-seven feet of the base are taken up by the spillway apron. The design provides for a maximum depth of 13 feet on the crest of the river, and a discharge of 500,000 cubic feet of water every second. The wasteway will carry

10,000 cubic feet per second. The working head is 92 to 95 feet. The power-houses will contain foundations for twelve 40,000-h.p. turbines of the single-runner type. The estimated primary power is 100,000 kilowatts, with total power of 300,000 kilowatts. The present steam-power plant may be operated in conjunction with the hydro-electric plant.

According to recent information, the control of the American nitrate plants is vested in three firms: Air Nitrates Corporation, interested in ammonia oxidation; the American Cyanamid Company, and the Air Reduction Company, both interested in cyanamide. Since there is, under present conditions, no considerable market for cyanamide or ammonium nitrate, it is proposed to adapt the plant to the manufacture of ammonium sulphate, the necessary sulphuric acid being available at the neighbouring works of the Tennessee Copper and Chemical Corporation.

The capacity of the Muscle Shoals plant may be estimated from the twelve carbide furnaces, each capable of producing carbide for 19,815 tons of dry nitrolim per annum. At full capacity, ten of these furnaces are working, two being in reserve for repairs, etc. The local steam-power plant, at present capacity, will operate eight furnaces, and as the power brought from the Government unit at the Warrior River Station of the Alabama Power Company is unduly expensive (0·2d. per kilowatt-hour), it is not proposed to operate more than eight furnaces until the cheap hydro-electric power (at 0·0375d. per kilowatt-hour) at present in process of installation is available. The intention is to operate the eight furnaces as follows:

(i.) Four furnaces for the manufacture of 76,000 tons of ammonium sulphate.

(ii.) One furnace for the manufacture of 19,900 tons of dry nitrolim, equivalent to 21,800 tons of hydrated and oiled cyanamide.

(iii.) Two furnaces for the manufacture of 19,650 tons of ammonium nitrate.

(iv.) One furnace for the production of cyanamide, ammonium sulphate, ammonium nitrate, or intermediate products, according to demand.

PLATE X.

WATER TUBES TO RJUKAN I.

To face p. 22[illegible]

When the hydro-electric power is available, the remaining two furnaces will be applied to the manufacture of the most advantageous product, possibly ammonium phosphate, which, under the name "Amophos," has been put on the market by the American Cyanamid Company as a very efficient and convenient fertiliser. It combines two essential plant foods—fixed nitrogen and phosphoric acid. Every effort will be made to cultivate the use of cyanamide and ammonium nitrate as fertilisers in place of the more familiar Chile nitre and ammonium sulphate, since the cost of production per unit of fixed nitrogen is less in these forms than in the form of ammonium sulphate. The sulphuric acid used in the manufacture of the latter is expensive, and so far from being useful as a plant food (as is nitric acid in ammonium nitrate or phosphoric acid in ammonium phosphate), it is believed to be positively injurious, rendering the soil unduly acid.

It is believed that the post-war price of ammonium sulphate in America will average above £16 5s. per ton. On the basis of nitrogen content alone, with ammonium sulphate (20·6 per cent. nitrogen) selling at the above price, hydrated and oiled cyanamide (19·2 per cent. nitrogen) would be worth about £15 2s. per ton, and ammonium nitrate (35 per cent. nitrogen) about £27 7s. per ton.

It is realised that the toxic properties of crude nitrolim and the deliquescent properties of ammonium nitrate will have to be overcome if their use is to be made popular with farmers, and a sufficient reduction in price will be necessary in order to induce farmers to take the trouble to face these difficulties. When cheap electric power is available, it is estimated that nitrogen in the form of ammonium sulphate would cost 45 per cent. more than in cyanamide at a possible selling price, and 17½ per cent. more than ammonium nitrate.

The disadvantage of cyanamide may be largely removed by hydration and oiling. M. Ferdinand Gros, in the Pyrenees, is said to have discovered a new process of treatment, in which a colloidal organic substance is used as a coating for the cyanamide grains. The treatment of ammonium nitrate is a more difficult problem. In Italy a process of soaking the seed grain in a solution of ammonium nitrate, followed by air-drying, has been tried, and is said to be very successful, but it is not known how this would work in damper climates. In the same country, ammonium nitrate recovered from ammunition has been coated with ground leucite (a mineral potassium aluminium silicate), the nitrogen content being reduced to 17 per cent., but the market for the product is limited.

When cheap electric power is available, and all royalties are eliminated, the following production costs have been stated to be possible under American conditions:

Product.	*Cost per Long Ton.*	*Cost per Metric Ton Nitrogen.*
	£	£
Cyanamide	5·71	28·1
Ammonium nitrate	15·92	45
Ammonium sulphate	10·18	49

Recent information indicates that synthetic nitrogen schemes in America are at present in abeyance. The manufacture of "Amophos" has apparently ceased, and the nitrates works at Muscle Shoals and Sheffield are shut down. There is little doubt that this is a temporary phase, and great activity in the near future may be expected. The synthetic ammonia plant at Sheffield is, it is said, at present being overhauled.

Cost of Fixation of Nitrogen as Cyanamide.

As regards the cost of fixation of nitrogen by the cyanamide process, much more detailed and reliable data are at hand than is the case with other processes. The method has been operated for some years, and has become established. The production of nitrogenous compounds by the cyanamide process exceeds the production by any other nitrogen-fixation method.

The total cost of fixation of nitrogen by the cyanamide process involves a considerable number of items. In the first place, there is the production of calcium carbide, and the separation of nitrogen from the air. Then there is the formation of crude nitrolim by the interaction of nitrogen and carbide. If the nitrolim is to be used directly as a fertiliser it requires to be crushed, hydrated, and oiled, but if ammonia or ammonium sulphate is to be made, the nitrolim must be decomposed by water at a high temperature in autoclaves and the ammonia distilled off.

The advantages claimed for the process are—

(i.) The relatively small power requirements as compared with the arc process (see, however, p. 201).

(ii.) The direct production of a solid nitrogenous fertiliser, thus avoiding the costs incurred in other processes for converting liquid products into solid marketable form.

(iii.) The production of a cheaper marketable form of combined nitrogen than that obtainable by any other established fixation process.

(iv.) The great adaptability of the process as regards the products obtainable.

Briefly expressed, the conclusions of the Nitrogen Products Committee on the economics of the cyanamide process are as follows: Cyanamide can be made for about £24 per metric ton of fixed nitrogen (equivalent to over 5 tons of actual cyanamide); on the basis of pre-war prices *plus* 50 per cent., the approximate factory costs would not exceed £6 8s. at a water-power site, or £7 at a steam-power station, using coal at 11s. 3d. per ton. Carbide can be manufactured for about £5 per ton, exclusive of the cost of packing.

The details of the estimate may now be given. It is to be remembered that these are based on pre-war prices *plus* 50 per cent., and that the alteration required by recent movements in coal prices may be readily made in the appropriate sections.

The probable production cost of carbide, exclusive of power, are given as follows:

	Carbide per Metric Ton. £
Lime: 950 kilogrammes at £0·75 per metric ton	0·712
Anthracite: 620 kilogrammes at £0·8 per metric ton	0·496
Electrodes: 25 kilogrammes at £15 per metric ton	0·375
Repairs	0·226
Labour and expenses	1·087
Depreciation at 8 per cent. on £3*	0·240
Total	£3·136

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* A capital cost of £3 per metric ton of carbide is adopted for the carbide factory on a pre-war basis.

The energy required in the production of 1 metric ton of carbide is 0·5 kilowatt-year of 8,400 to 8,500 hours. To the above figure of £3·136 must therefore be added half the cost of electrical energy per kilowatt-year. With electrical energy at various prices, the following costs of carbide (unpacked) would therefore result:

	£	£	£	£
Cost of energy per kilowatt-year	1·2	3·75	6	8
Cost per metric ton carbide	3·74	5·01	6·14	7·14

On the basis of a loss of 30 per cent. of the nitrogen in the fixation process, the cost of conversion of carbide to cyanamide is arrived at as follows:

The quantity of carbide required per ton of nitrogen fixed is about 4 tons, or 0·8 ton of carbide per ton of cyanamide of 20 per cent. nitrogen content.

The over-all power requirement amounts to 2·3 kilowatt-years of 8,400 to 8,500 hours per metric ton of nitrogen fixed, or 0·46 kilowatt-year per metric ton of cyanamide (20 per cent. nitrogen content). As 0·5 kilowatt-year is required for the carbide stage, and as 4 tons of carbide are required to produce 1 ton of fixed nitrogen as cyanamide, the power required for the conversion of carbide to cyanamide alone will be— $2·3 - 4 \times 0·5 = 0·3$ kilowatt-year per metric ton of nitrogen fixed, or 0·06 kilowatt-year per metric ton of cyanamide (20 per cent. nitrogen).

The capital cost of the cyanamide conversion factory is taken as £4·5 per metric ton of cyanamide, or £22·5 per metric ton of fixed nitrogen, per annum, including the cost of nitrogen and packing plants, for discontinuous working (*cf.* p. 196). The pre-war capital cost per metric ton of cyanamide (20 per cent. nitrogen) per annum will therefore be—

		£
Carbide section	£0·8 × £3 =	2·4
Cyanamide section		4·5
Total		£6·9

or £34·5 per metric ton of nitrogen fixed per annum.

The cost of the power-station, on the basis of the Nitrogen Products Committee estimate (p. 261) of £10·26 per kilowatt-year, would be 0·5 × £10·26 = £5·13 per metric ton of cyanamide per annum, and the total cost of the power and chemical sections, up to the stage of raw cyanamide, would therefore be £6·9+£5·13=£12·03 per metric ton of cyanamide (20 per cent. nitrogen), or £60·15 per metric ton of fixed nitrogen, per annum.

The probable conversion cost of carbide to cyanamide is given as follows:

	Cyanamide 20 per Cent. Nitrogen per Metric Ton.
Nitrogen, electrodes, labour, repairs, and expenses ..	£1·40
Depreciation at 8 per cent. on £4·5	£0·36
Total ..	£1·76

amounting to £8·8 per metric ton of nitrogen fixed.

The production cost of raw cyanamide, excluding power, in a large factory favourably situated as regards raw materials will then be as follows:

	Cyanamide 20 per Cent. Nitrogen per Metric Ton.
Raw carbide: 0·8 metric ton at £3·136 per ton, exclusive of power	£2·51
Cost of conversion, exclusive of power	£1·76
Total ..	£4·27

or £21·35 per metric ton of fixed nitrogen, unpacked. With an allowance of 5 per cent. interest on a capital of £6·9, the total costs are £4·615 and £23·07 respectively.

To this cost must now be added the cost of energy, of which 0·46 kilowatt-year is required. With energy at various prices, the following figures are obtained per metric ton of cyanamide (20 per cent. nitrogen), inclusive of capital charges, but exclusive of interest:

	£	£	£	£
Cost of energy per kilowatt-year ..	1·2	3·75	6	8
Cost per metric ton cyanamide ..	4·82	6·00	7·03	7·95
Cost per metric ton fixed nitrogen ..	24·10	30·00	35·15	39·75

The pre-war price of cyanamide in this country, containing 18 per cent. nitrogen, was £10·62 per long ton, or £58·08 per metric ton of fixed nitrogen.

All the above figures refer to the discontinuous processes; the costs by the continuous process (p. 229) are lower by about 20 per cent. The advantages of the continuous process claimed are—

(i.) Lower capital cost for the chemical plant.
(ii.) Lower consumption of carbide per ton of cyanamide produced.
(iii.) Lower consumption of energy per ton of cyanamide produced.
(iv.) Reduction in charges for labour and repairs.

These economies may be appreciated by comparing the requirements in materials and energy of the continuous process with those given for the discontinuous process:

REQUIREMENTS PER METRIC TON OF NITROGEN FIXED.

	Continuous Process.	*Discontinuous Process.*
Carbide	3·625 metric tons.	4 metric tons.
Energy	1·97 kilowatt-year.	2·3 kilowatt-year.
Capital cost of carbide cyanamide factory	£17·58 per annum.	—
Over-all cost of complete factory	£25·25 ,,	£34·5
Total capital cost of power and chemical sections	£45·45	£60·15

The cost of the plant for the after-treatment of the raw cyanamide (hydration and oiling) is said to amount to only £0·9 per metric ton of fixed nitrogen per annum.

The production costs, *exclusive of power*, for the continuous process are as follows, the previous figure for carbide (p. 223) being adopted, and with labour at £0·28 per shift. The over-all costs given are exclusive of packing and interest on capital:

	Cyanamide 19·5 per Cent. Nitrogen per Metric Ton. £
Carbide: 0·707 ton at £2·955 per ton, enclusive of power	2·089
Nitrogen, exclusive of power	0·106
Sundry materials	0·192
Electrodes at £14·62 per ton	0·074
Wages at £0·28 per shift	0·100
Repairs: cyanamide section only	0·279
General charges	0·110
Depreciation at 4 per cent. on buildings and 10 per cent. on plant	0·297
Total	£3·247

or £16·65 per metric ton fixed nitrogen. The equivalent cost of cyanamide with 20 per cent. nitrogen is £3·33 per metric ton, as compared with £4·27 for the discontinuous process.

After-treatment with water and oil reduces the nitrogen content of the cyanamide from 19·5 to 17·5 per cent., and costs £1·13 per metric ton of fixed nitrogen in the cyanamide, or £0·2 per metric ton of final product containing 17·5 per cent. nitrogen.

The cost of the 0·384 kilowatt-year of energy required per metric ton of cyanamide (19·5 per cent. nitrogen) must now be added to the £3·247 to give the cost per metric ton of this product.

	£	£	£	£
Cost of energy per kilowatt-year	1·2	3·75	6	8
Cost of cyanamide (19·5 per cent. nitrogen) per metric ton ..	3·708	4·687	5·551	6·319
Cost of fixed nitrogen per metric ton	19·01	24·04	28·42	32·39

The Committee are of the opinion that the operating costs as given in the above estimates should be increased by 5 per cent. to allow for contingencies.

The cost of energy has a much smaller influence on the manufacturing costs in the cyanamide process than is the case in the arc process. Every additional £1 in the cost of energy per kilowatt-year affects the production costs by the *continuous* process to the extent of £0·381 per metric ton of cyanamide of 19·5 per cent. nitrogen content, or £1·97 per metric ton of fixed nitrogen. In the *discontinuous* process the corresponding figures are £0·46 and £2·3 respectively.

We have next to examine the costs of production of ammonia and ammonium sulphate from cyanamide. The process of manufacture is a comparatively simple one, involving the treatment of the finely ground cyanamide with superheated water in autoclaves. The efficiency of conversion in the cyanamide —> ammonia stage appears to be about 95 per cent.—*i.e.*, of every 100 units of fixed nitrogen in the cyanamide as charged to the autoclaves, 95 units are recovered in the form of ammonia.

With this conversion efficiency, 4·33 tons of cyanamide containing 20 per cent. of nitrogen are required for the production of 1 ton of ammonia (anhydrous), and 5 tons of dry residue would be formed (calcium carbonate and graphite). Since the actual sludge from the autoclaves would contain water about 40 per cent. in excess of the dry residue, the actual weight of wet sludge for disposal per ton of ammonia will be about 7 tons. The problem of disposal of this caustic sludge is one of the great difficulties of the cyanamide process. The boots and clothes of the workmen, and the hoofs of horses, are rapidly corroded by contact with autoclave sludge. Proposals to dry the sludge, and use the calcium carbonate and graphite for reconversion into carbide, or to extract the graphite, appear to have had no practical application, although the conversion of the sludge into calcium nitrate, leaving graphite in a readily filterable condition, by the process of the authors (p. 322) seems to offer possibilities in this direction.

The capital cost of autoclaving cyanamide has been reliably stated to be £6·12 per metric ton of combined nitrogen per annum in the form of ammonia.

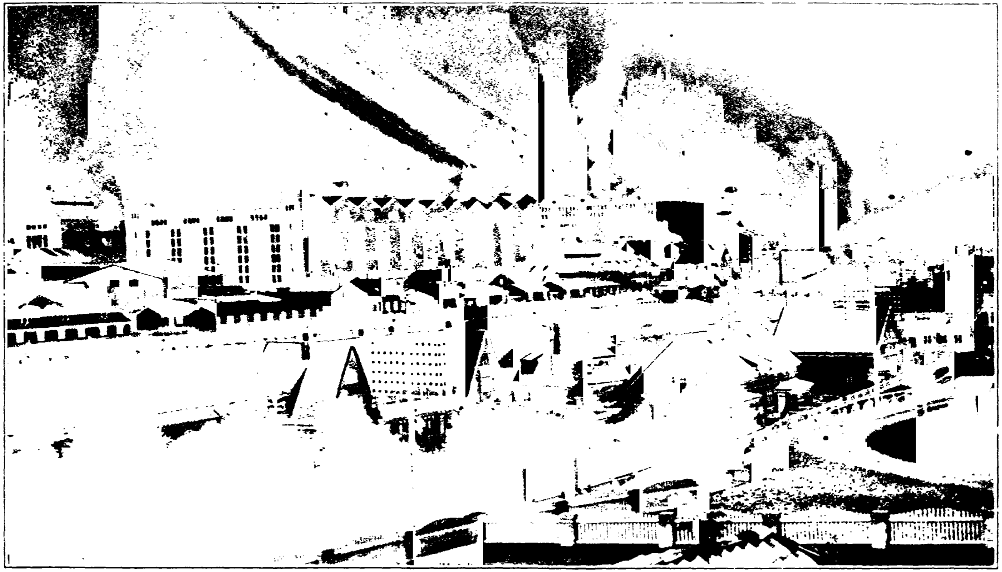
The conversion cost of £4·05 per metric ton of combined nitrogen in the form of ammonia, based on American practice, is adopted by the Nitrogen Products Committee, although they point out that recent large-scale practice in that country is expected to halve this cost.

The energy requirements of the conversion process are modest, and amount to about 130 kilowatt-hours per metric ton of ammonia, or 0·018 kilowatt-year per metric ton of combined nitrogen in the form of ammonia. With energy at 0·25d. per unit, the cost of the energy required in the conversion of cyanamide into ammonia would be: 0·25d. × 130 = £0·135 per metric ton of ammonia, or £0·164 per metric ton of combined nitrogen.

The cost of conversion, exclusive of loss of ammonia and interest on capital, would thus be £4·05 + 0·164 = £4·214 per metric ton of nitrogen, or £3·475 per metric ton of ammonia.

The over-all capital cost of a complete ammonia factory, *via* cyanamide, will be the capital cost of the cyanamide factory (p. 224) *plus* £6·12 per metric ton of combined nitrogen per annum conversion cost. The capital cost of the power-station will be increased by the cost for generation of 0·018 kilowatt-

PLATE XI.



RJUKAN I. AND II.: GENERAL VIEW.

To face p. 228.

year per metric ton of combined nitrogen per annum. For the *discontinuous* process the capital cost (over-all), allowing 5 per cent. on the capital cost of the carbide cyanamide section to cover losses in conversion, will be—

I. Carbide cyanamide section $(1{\cdot}05\times 34{\cdot}5)+$conversion $6{\cdot}12=$ £42·34.

II. Power section, carbide cyanamide $1{\cdot}05\times 2{\cdot}3\times$ £10·26 +conversion $0{\cdot}018\times$ £10·26 = £24·96.

∴ total = £42·34 + £24·96 = £67·3 per metric ton combined nitrogen per annum, or £55·44 per metric ton of ammonia per annum.

For the continuous process the corresponding figures are £54·03 and £44·5 respectively.

The *production costs* of ammonia by the cyanamide process may be obtained, for energy at different prices, by adding to the cost of carbide cyanamide equivalent to 1 metric ton of combined nitrogen (*plus* 5 per cent. for conversion losses) at the various prices (p. 225), the cost of conversion to ammonia (£4·050 per metric ton nitrogen), and the cost of 0·018 kilowatt-year of energy, at the various prices, as required for the conversion.

The cost of fixing 1 metric ton of combined nitrogen in the form of ammonia, with production of packed ammonium sulphate, is estimated at £8·650, and thus the cost of production of ammonium sulphate *via* cyanamide may be estimated.

Continuous Cyanamide Process.—Carlson (Brit. Pat. 123,796) has introduced a continuous process used by the Stockholms Superfosfat Fabriks Aktiebolag at Ljunga Verk, in which calcium carbide, intimately mixed with an "indifferent substance" which prevents fusion (in practice quicklime is said to be used), and a catalyst such as calcium chloride or fluoride, is passed down a multistage furnace by intermittent raking. Preliminary heating is effected by an electric arc in the top of the furnace, but the reaction when started is exothermic. Nitrogen is passed in at the bottom, and it is claimed that 80 per cent. of the nitrogen used is absorbed. The power consumption is about 1,500 kilowatt-hours per metric ton of nitrogen fixed, while 3 to 5 kilogrammes of electrodes are consumed per metric ton of cyanamide. 720 to 730 kilogrammes of calcium carbide of 300 litres are required per metric ton of cyanamide. The output is 20 to 25 tons of cyanamide per furnace per day. It is claimed that the product is porous and coke-like in nature, being more easily crushed than cyanamide obtained by other processes, and contains 20 to 21 per cent. of nitrogen. The annual output at Ljunga Verk is 20,000 metric tons of cyanamide.

Fixation of Nitrogen as Nitrides: the Serpek Process.—Many elements, such as lithium, calcium, magnesium, and boron, absorb nitrogen when heated, forming nitrides—*e.g.*, Li_3N and Ca_3N_2—which are decomposed by water or steam with evolution of ammonia: $Ca_3N_2+6H_2O=3Ca(OH)_2+2NH_3$. Owing to the difficulty of reducing the hydroxides again to metals, the use of such substances as intermediaries in the fixation of atmospheric nitrogen has not found industrial application. A more promising reaction is the formation of aluminium nitride from a mixture of alumina and carbon heated to a very high temperature in nitrogen: $Al_2O_3+3C+N_2=2AlN+3CO$. The nitride can be decomposed by heating with water and a little alkali under pressure: $AlN+3H_2O=Al(OH)_3+NH_3$. This was applied in the Serpek process, which was worked for a time in the Savoy, but was ultimately abandoned. The solids were heated in a revolving tubular furnace with an electrical resistance heater composed of a number of carbon rods embedded in the walls of the tube. A temperature of 1,500° to 1,800° C. is necessary, and great demands are made on the refractories composing the furnace. The figures stated for the process are attractive, the total power consumption being given as only 10 to 12 kilowatt-hours per kilogramme N fixed. Further, the alumina left after the decomposition of the nitride is suitable for the manufacture of aluminium, and by using bauxite as the initial material the process might be combined with the manufacture of aluminium. It is understood that experiments are in progress by the American Aluminium Company, the chief problem being the discovery of a suitable refractory material for the furnace. It is not known with what success this work has been attended.

In a more recent account of his process, Serpek (*Zeitschr.*

für. kompr. und flüss. Gase, 1914, **17**, 57) refers to a modification in which the charge in powder form is dropped through an atmosphere of nitrogen in a smaller type of furnace (4 metres high and 1·5 métres wide). See also Toniolo, *Giornale di Chimica Industriale ed Applicata*, July to August, 1921.

Fixation of Nitrogen as Cyanides.—Dawes in 1835 found that cyanides were produced in the blast furnace, and the researches of Bunsen and Playfair about 1840 showed that these cyanides were formed by the interaction of atmospheric nitrogen with potassium and carbon compounds in the furnace. If nitrogen is passed over a mixture of potassium carbonate and carbon at a high temperature potassium cyanide is formed; with sodium carbonate the yield is very small. The process was used on a small scale at Grenelle and at Newcastle-on-Tyne, but owing to the action of the materials on the vessels at the high temperatures the method was discontinued. In 1862 Margueritte and De Sourdeval found that if barium carbonate or hydroxide is used instead of potash the yield is very much improved. The barium cyanide formed may be decomposed by treatment with steam at 300° with evolution of ammonia, the barium hydroxide being regenerated: $Ba(CN)_2+4H_2O=2NH_3+Ba(OH)_2+2CO$. The process was worked by Mond for a time, but was later abandoned. Readman used the same process, with electrical heating, between 1899 and 1907 at the works of the Scottish Cyanide Company. J. E. Bucher (*J. Ind. Eng. Chem.*, 1917, **9**, 233; *Met. and Chem. Eng.*, 1916, **14**, 543) claims that nitrogen can be economically fixed as sodium cyanide by heating an intimate mixture of equal weights of sodium carbonate, coke, and metallic iron, formed into briquettes, at 920° to 950° in a stream of nitrogen or producer gas. The resulting product is said to contain 20 to 30 per cent. of sodium cyanide, representing 5·7 to 8·7 per cent. of combined nitrogen, and may be decomposed by steam to form ammonia—

$$Na_2CO_3+4C+N_2=2NaCN+3CO-138{\cdot}5\text{ kg.-cal.}$$
$$NaCN+2H_2O=H.COONa+NH_3.$$

Bucher proposes to form the carbon directly in the mass by the reaction $2CO=CO_2+C$ at high temperatures in presence of the iron. All the essential features of Bucher's process were patented by Adler in 1880, but the rights were allowed to lapse. The United States Government have made careful investigations of the process. A large plant was said to be ready to begin operations at the time of the Armistice.

Clancy (U.S. Pat. 1,329,652; *Met. and Chem. Eng.*, 1920, **22,** 856) finds that, of the many compounds present in the reaction product of the Bucher process, only sodium cyanide is soluble in liquefied ammonia. The extracted residue, when returned to the process, seems to have an improved catalytic action. Air must be excluded, or cyanates, also soluble in liquid ammonia, are formed.

Mount (U.S. Pat. 1,329,721; *Met. and Chem. Eng.*, 1920, **22,** 709) has devised a continuous process, briquettes of the charge being fed to a vertical retort, treated countercurrently with nitrogen, and kept at 1,000° C. Cyanide, as formed, binds the briquettes, and on reaching the cooler part of the retort a solid mass is formed, which is broken up and passed to a cooler.

Thompson (*Met. and Chem. Eng.*, 1922, **26,** 124) states that a pure form of carbon is necessary. Coke gives poor results. The materials, consisting of precipitated iron oxide, carbon, and soda ash, are finely ground, and if the briquettes after heating contain 80 per cent. of iron and total alkali, no binder is necessary. It is suggested that 35 tons of briquettes should give 7 tons of sodium cyanide.

SECTION III

THE ARC PROCESS

THE principle of the so-called "arc process" for the fixation of atmospheric nitrogen is the following: When atmospheric air or other mixtures of nitrogen and oxygen are heated to a sufficiently high temperature, combustion of the nitrogen occurs, with the formation, in the first instance, of nitric oxide, NO : $N_2+O_2 \rightleftharpoons 2NO$. The process is reversible, and a state of equilibrium may be set up at each temperature (see p. 15). A large amount of heat is absorbed in this reaction, so that it differs entirely from ordinary processes of combustion, in which heat is evolved. This is, of course, a necessary condition for the existence of the atmosphere at all; if nitrogen and oxygen could combine with the evolution of heat, the smallest flame presented to the atmosphere would lead to its ignition, and the earth would be deluged with nitric acid, the product of the combustion in the presence of water. Owing to the absorption of heat in the combustion, however, it is necessary to supply continually large quantities of heat to the gases, otherwise the process stops. It is also necessary, in order to get appreciable yields, to work at a very high temperature—say 2,000° to 3,000° C. Such high temperatures are practically only reached in the electric arc, which has a temperature of at least 3,000° C.

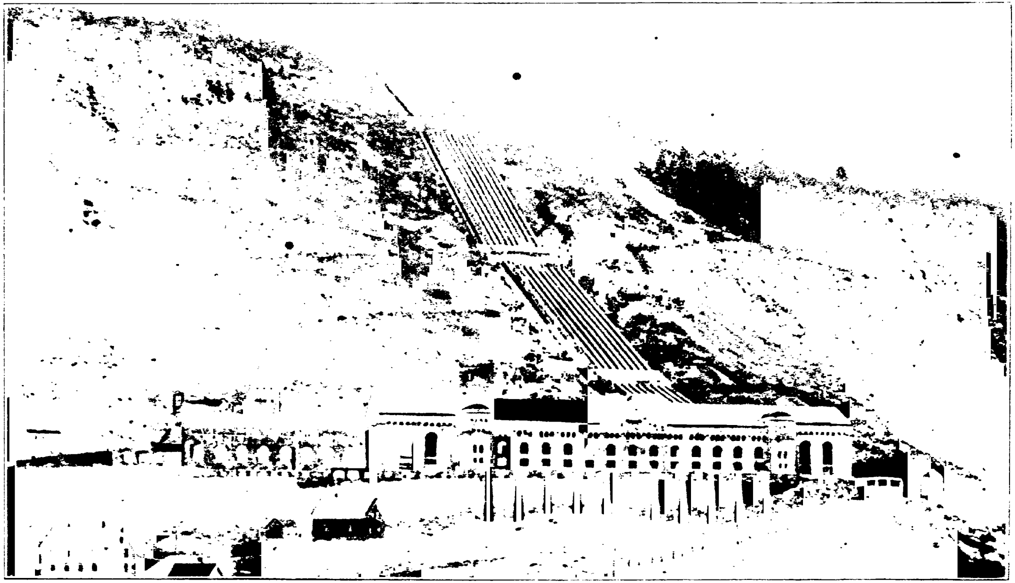
It is obvious that, on the principle of the combustion of air at a very high temperature, an industrial process for the fixation of nitrogen can be founded, since the product, nitric oxide, can be converted simply by the excess of oxygen in the air, together with water, into nitric acid, which is one of the most useful forms of combined nitrogen. The technical realisation of the process proved, however, to be by no means simple. In the first place, some type of electric arc must be applied which presents a large surface to the air brought in contact with it, and is at the same time stable—*e.g.*, not liable to be extinguished by the blast of air. In the second place, some means of cooling the gases rapidly after they have been exposed to the intense heat of the arc must be devised, since, if the gas is cooled down slowly, the nitric oxide which was formed at the high temperature is almost completely decomposed again as the temperature falls, on account of the reversible character of the reaction. When, however, the temperature is very rapidly lowered from 3,000° to about 1,000° C., the nitric oxide will not be allowed sufficient time to undergo decomposition, since this process is not instantaneous, but requires a finite time, which is very small, it is true, at very high temperatures, but becomes more and more appreciable as the temperature falls, until at and below 1,000° C. the rate of decomposition of nitric oxide has become so slow as to be inappreciable. The gas then behaves as though it had no tendency whatever to undergo decomposition. The conditions may be compared roughly with those under which a candle, which is a combustible body, can exist indefinitely in the presence of air unless heat is applied to the wick. It is only when the combustible is raised to a sufficiently high temperature that the reaction occurs at an appreciable rate.

The amount of nitric oxide formed when air is raised to a very high temperature and then rapidly cooled, as described, is from 1 to 2 per cent. by volume.

In the descriptions of the synthetic ammonia and cyanamide processes we have pointed out that, although much preliminary work was done by various experimenters, the real establishment of the technical processes was due to German chemists. The first steps in the establishment of the process of the fixation of nitrogen in the electric arc, the one process unsuited to present British conditions, were made by British scientific investigators. Henry Cavendish, in 1784, noticed that when a mixture of oxygen and nitrogen gases was exposed to a continuous stream of electric sparks in a tube confined over potash solution, the gas gradually disappeared and the potash was converted into potassium nitrate, or nitre.

During the last century the late Lord Rayleigh was occupied in purely academic researches on the densities of

PLATE XII.



RJUKAN I. POWER STATION. EXTERIOR.

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gases. In these he introduced refinements in previous methods, and was thus enabled to reach great accuracy. These experiments had no technical object, and would doubtless have been regarded with disfavour by the severely practical type of mind which is so common in British business circles. In the course of this work Lord Rayleigh made a curious observation. In 1894 he found that nitrogen gas obtained from the atmosphere was slightly but distinctly heavier than pure nitrogen obtained from chemical substances. The weight of the "chemical" nitrogen was 1·25107, whilst that of the "atmospheric" nitrogen was 1·25718. Such a difference, which could only have been detected by the accurate methods used by Lord Rayleigh, did not escape such an acute experimenter. It was necessary to find an explanation for the difference. Lord Rayleigh then remembered the old experiment of Cavendish, and in reading Cavendish's memoir he was struck by the mention of another curious fact. Cavendish, who was an experimenter of the same calibre as Lord Rayleigh, had noticed that in sparking the two gases over potash there was never complete absorption, but a slight residue of gas was always left which could not be induced to enter into chemical combination with oxygen. Lord Rayleigh saw that, if it was assumed that atmospheric nitrogen contains a small amount of another gas, slightly heavier than nitrogen, which had not been noticed by previous observers (except Cavendish), the higher density of atmospheric nitrogen was readily explicable.

The analysis of air had, however, been carried out by hundreds of chemists since the time of Cavendish, and some of the analyses were of great accuracy. It was, therefore, hardly possible that in so common a material as air, which had been the subject of so many experiments, any previously unnoticed constituent could be present. At the same time, this was the most reasonable explanation. Lord Rayleigh and Sir William Ramsay then joined forces, with the result that ultimately no less than five entirely new gases, all elements, were discovered in atmospheric air. These are the inactive elements—helium, neon, argon, krypton, and xenon. They form no compounds with any other elements.

In the course of this work, and merely as a side-issue, Lord

Rayleigh laid the foundations of the modern nitrogen-fixation industry. In order to examine the minute residue of gas noticed by Cavendish, Lord Rayleigh caused the experiment to be performed on a much larger scale. He used, instead of the sparks from a frictional electric machine as employed by Cavendish, a powerful electric arc burning inside a glass globe containing a mixture of oxygen and nitrogen. The inside of the globe was kept cool by a fountain of caustic soda solution, which also absorbed the oxides of nitrogen formed in the reaction. A mixture of sodium nitrite and sodium nitrate was produced:

(1) $N_2+O_2=2NO$ (oxidation in the arc).
(2) $2NO+O_2=2NO_2$ (secondary oxidation, with formation of brown fumes of NO_2).
(3) $2NO_2+2NaOH=NaNO_2$ (sodium nitrite)$+NaNO_3$ (sodium nitrate)$+H_2O$.

Lord Rayleigh obtained a yield of nitric acid of 46 grammes per kilowatt-hour expended. In the most modern plant, 62 grammes are obtained. The fixation of nitrogen, it will be seen, was not the primary object of the experiment, which was to remove the oxygen and nitrogen of air together, leaving the new gases.

From beginning to end the magnificent work of Lord Rayleigh was "academic." We may therefore be pardoned if we once more insist that, almost without exception, all the great discoveries of chemical industry have been made by men working in the cause of pure science, and not by squads of employees working in technical laboratories under direction. There is no more important lesson for the business man than the work of Lord Rayleigh. The latter was an example of a type of scientific investigator in which the English may take a peculiar pride. Born, not raised, to the peerage, Lord Rayleigh devoted his magnificent gifts to the cause of science, and one of his many achievements is the foundation of the nitrogen-fixation industry. It is true that the name of Lord Rayleigh is not usually prominent in the descriptions given in technical manuals of this industry; this is merely the result either of ignorance or of oversight.

The first attempt to put the discovery of Rayleigh on a technical basis was made by McDougall and Howles, in Manchester, in the year 1899. These two experimenters have the honour of being the first to show the possibility of the technical utilisation of the scientific work of Lord Rayleigh. Neither their process nor the later and more elaborate plant of Bradley and Lovejoy at Niagara Falls was a commercial success. The credit of inventing, in 1903, a really successful technical method for the fixation of nitrogen in the electric arc belongs to two Norwegians—Dr. Birkeland, Professor of Physics at the University of Christiania (an "academic" man of science), and Dr. Samuel Eyde, an engineer. From the joint efforts of these two men, who were sustained by a splendid optimism and a faith in their ideas which have been abundantly justified, the modern arc process in Norway has developed. At present some 300,000 h.p. are expended on nitrogen fixation in Norway.

Independently, a successful arc furnace was evolved by Dr. Schönherr, working for the Badische Company, and by Pauling, at Innsbrück, in the Austrian Tyrol. All these furnaces are at present in actual operation, the Birkeland-Eyde to the largest extent.

The three processes differ somewhat considerably in principle. In the Birkeland-Eyde process an electric arc is struck between water-cooled copper electrodes with the extremities close together, and the arc is then spread by means of a powerful magnetic field at right angles to the path of the arc. The poles of a strong electromagnet are placed one on each side of the electrodes to provide a constant magnetic field. The arc is produced by an alternating current of high voltage (6,500 volts), and each successive small arc is spread by the magnetic field until it breaks and a new arc starts. By reason of the alternating nature of the current in the arc, the latter is spread alternately on one and on the other side of the electrodes, and the alternations succeed one another so rapidly that an apparently continuous sheet or circular disc of flame, about 6 feet in diameter, is produced. This is enclosed in a circular iron box, lined inside with refractory bricks, with inlet ports for air on each side of the electric disc, and an outlet for the gas at the bottom. Air is blown or drawn through the chamber, and sweeps over each side of the arc. The latter exposes a large surface, and the air in contact with it is probably heated to about 3,000° C.

Nitric oxide is formed, and the intensely hot gas then sweeps into a large iron tube lined inside with firebricks. In this its temperature is quickly reduced to about 1,000° C. The gas then passes through the firebox of a tubular steam boiler, where further cooling to about 250° C. occurs, with production of more steam than is used in the whole works. The gas is next cooled to about 50° C. in large aluminium pipes cooled by water, and then passes through a large empty iron tower, in which the oxidation of the nitric oxide to nitrogen dioxide occurs: $2NO+O_2 \rightleftharpoons 2NO_2$. With the dilute gas this process of secondary oxidation requires about two minutes to attain practical completion.

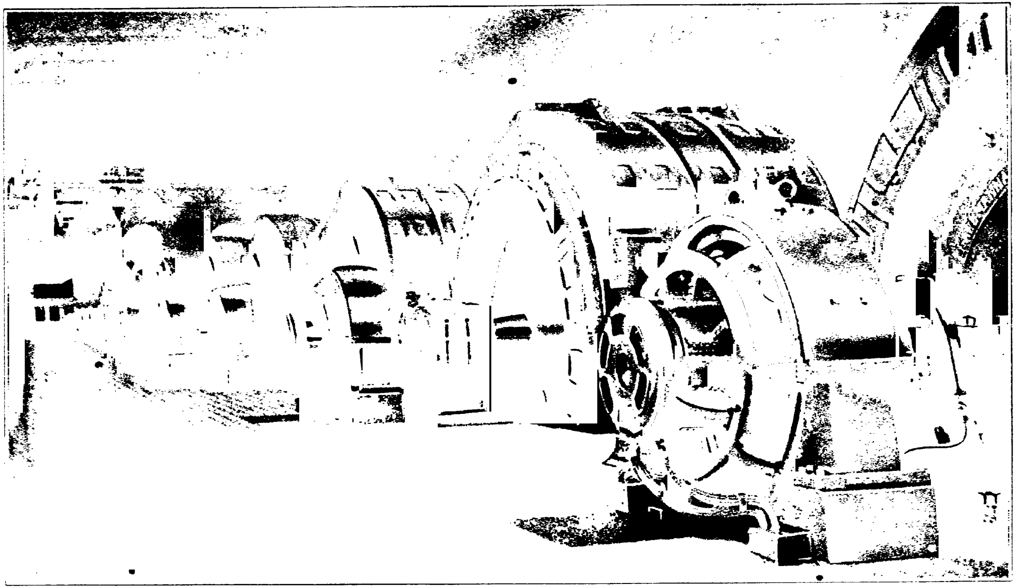
The gases finally pass through a series of enormous granite absorption towers, 65 feet high and 20 feet diameter, built up of slabs of Norwegian granite, and packed with broken quartz over which water trickles. The nitrogen dioxide is absorbed as dilute nitric acid:

(1) $2NO_2+H_2O=HNO_3+HNO_2$ (absorption reaction).
(2) $2HNO_2=NO+NO_2+H_2O$ (decomposition in solution).
(3) $2NO+O_2=2NO_2$ (oxidation in gas space).

About 85 per cent. of the total nitrogen dioxide absorbed is obtained in the form of nitric acid of 30 per cent. strength. The gas passing from the water-absorption towers is passed through an iron tower packed with quartz, over which a solution of sodium carbonate trickles. Sodium nitrite, $NaNO_2$, which is used in the manufacture of dyes, and sodium nitrate, $NaNO_3$, are obtained by evaporation of the solution. The remaining 15 per cent. of oxides absorbed are recovered in this form. It is found in practice that about 2 per cent. of the oxides of nitrogen always escape absorption and are lost; the remaining 98 per cent. are absorbed in the proportion of 85 of nitric acid and 15 of nitrite and nitrate of sodium.

The 30 to 40 per cent. *nitric acid* may be concentrated by

PLATE XIII.



RJUKAN I.: POWER STATION INTERIOR.

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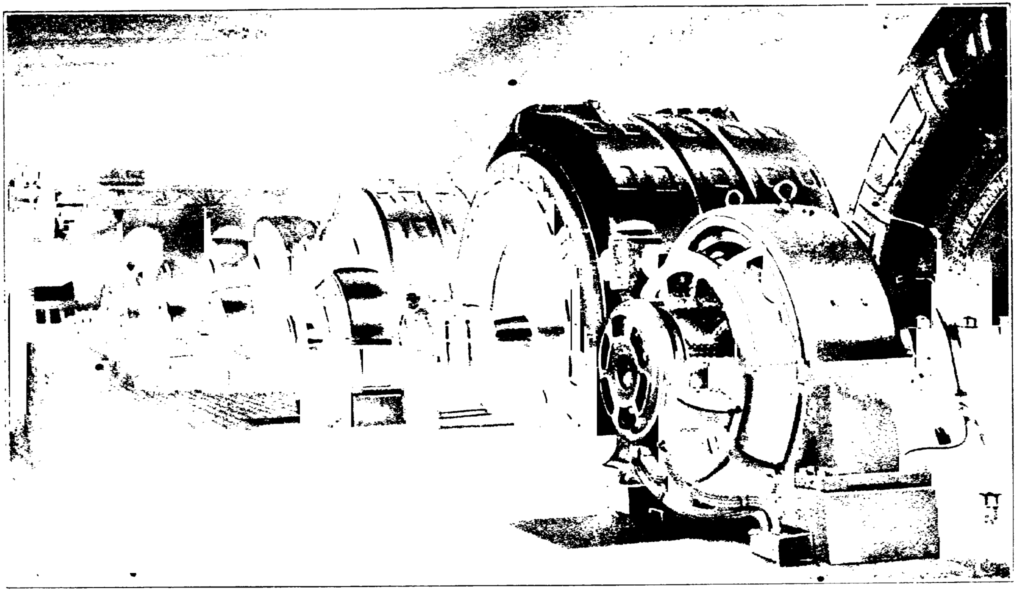
The 30 to 40 per cent. *nitric acid* may be concentrated by

PLATE XIII.



RJUKAN I.: POWER STATION. INTERIOR.

To face p. 138.

distilling it with concentrated sulphuric acid, or it may be converted into nitrates. If the dilute acid from the towers is run into granite tanks filled with broken limestone, calcium nitrate is formed, carbon dioxide gas being evolved:

$$CaCO_3 + 2HNO_2 = Ca(NO_3)_2 + CO_2 + H_2O.$$

The solution of *calcium nitrate* is evaporated, and sets to a mass known as "Norge saltpetre," used as a fertiliser. It is sent out in wooden barrels (see later). The nitric acid may also be neutralised with ammonia solution, which is made by the cyanamide process, to form *ammonium nitrate*, NH_4NO_3, which is crystallised by evaporation. Sodium nitrate may also be made by neutralising with soda ash, imported from English alkali works.

The processes of Schönherr and of Pauling do not call for detailed description. In the former the arc is produced in a long vertical tube, and the air is admitted through apertures, so that it moves up the tube in a spiral, alternately striking the arc and the cool walls of the iron tube in which the arc burns. The arc flame is in this case noiseless, whilst the disc in the Birkeland-Eyde furnace emits a loud and unpleasant rattling noise. The subsequent treatment of the gas leaving the Schönherr furnace is the same as in the Birkeland-Eyde process. Some Schönherr furnaces are in operation in the Norwegian works, and they are also used to some extent in Germany.

In the Pauling process an arc is struck between two horn-shaped electrodes which approach at the lower part of the horns. The arc is then blown upwards between the horns by a powerful blast of air directed upwards in the space between the electrodes. When the arc reaches the top of the horns it becomes so elongated that it breaks, and a new arc starts again below. Through this rapid succession of arcs the air passes, and the gases are then treated in the same way as in the other processes, for the production of nitric acid. In the original Pauling process iron electrodes were used. The researches of Dr. Rossi, who employs a modified Pauling process, showed that in this case the yield is small, since the nitric oxide is decomposed on cooling in contact with particles of iron oxide produced from the electrodes. By using cooled aluminium electrodes, Rossi was enabled to obtain much better yields. The Pauling furnaces are much smaller than those of the Birkeland-Eyde or Schönherr type, and are particularly adapted to localities where power is obtainable only intermittently, as in the "off-load" periods of large metropolitan electric generating stations.

Speaking broadly, one may say that for large undertakings the Birkeland-Eyde and Schönherr furnaces are about equally efficient, whilst for small works the Pauling furnace is most convenient and economical. In all cases the gases contain about 1 per cent., or slightly over, of nitric oxide.

The most important commercial product of the arc factories is calcium nitrate ("nitrate of lime"), which is used as a fertiliser.

Statistics of Production of Calcium Nitrate in Norway by the Arc Process.

Year.	*Production in Metric Tons.*		*Consumption in Metric Tons (Approximately).*
	Calcium Nitrate.	*Combined Nitrogen.**	*Calcium Nitrate.*
1907	1,601	208	215
1908	5,102	663	470
1909	11,953	1,554	970
1910	18,569	2,414	1,860
1911	13,152	1,709	1,967
1912	36,468	4,741	3,721
1913	73,214	9,518	5,500
1914	82,000	10,700	7,500
1915	48,000	6,200	9,500
1916	61,000	7,900	15,000
1917	72,000	9,400	36,500
1918	105,000	13,600	51,000
1919	109,000	14,200	45,000
1820	—	—	110,000

* On the basis of 13 per cent. combined nitrogen in the calcium nitrate. The figures for 1914-1919 are taken from Report on the Commerce and Industry of Norway, Cmd. 839, 1920. The consumption in 1920 is from the Nitrate Trading Company. The price of calcium nitrate sold for fertiliser purposes in England in December, 1920, was £23 15s. per ton, equivalent to £179 8s. per ton of combined nitrogen.

The striking feature of the above table is the increase in home consumption in Norway as a fertiliser. In 1919 this amounted to ten times the pre-war figure.

With reference to the use of nitrate of lime as a fertiliser, we may mention the interesting brochure entitled "Le Nitrate de Norvège, son emploi," by M. de la Vallée Poussin, issued by the Société norvégienne de l'azote, Paris, 1913.

The production of nitric acid in the arc process is very small in comparison with the total electrical energy expended. In all three types of furnace it amounts to about 61 grammes of nitric acid (calculated as 100 per cent. HNO_3) per kilowatt-hour, measured at the station switchboard, with full allowance for losses during absorption and concentration. In other units this amounts to an expenditure of—

1·87 kilowatt-years per metric ton (1,000 kilogrammes) of nitric acid;
8·41 kilowatt-years per metric ton of nitrogen fixed;
2·55 h.p.-yrs. per long ton (2,240 pounds) of nitric acid;
11·45 h.p.-yrs. per long ton of nitrogen fixed.

(In all cases 1 year is taken as 8,760 hours; 1 kw.=1·341 h.p.; 1 long ton=2,240 pounds; 1 metric ton=2,205 pounds.)

On account of this large consumption of energy, the arc process can be operated economically only in localities where very cheap and (except when the Pauling furnace is used) continuous sources of electrical energy are available. The cheapest source of energy at present known is water power. In Norway the cost per kilowatt-year of electrical energy from water power is about £1·2; in England, with coal as the source of energy, the corresponding cost is about £6 to £8, so that there seems little prospect of successful operation of arc processes with coal in this country. The cost of water power with continuous working at Kinlochleven and Foyers is estimated at 34s. per h.p.-year.

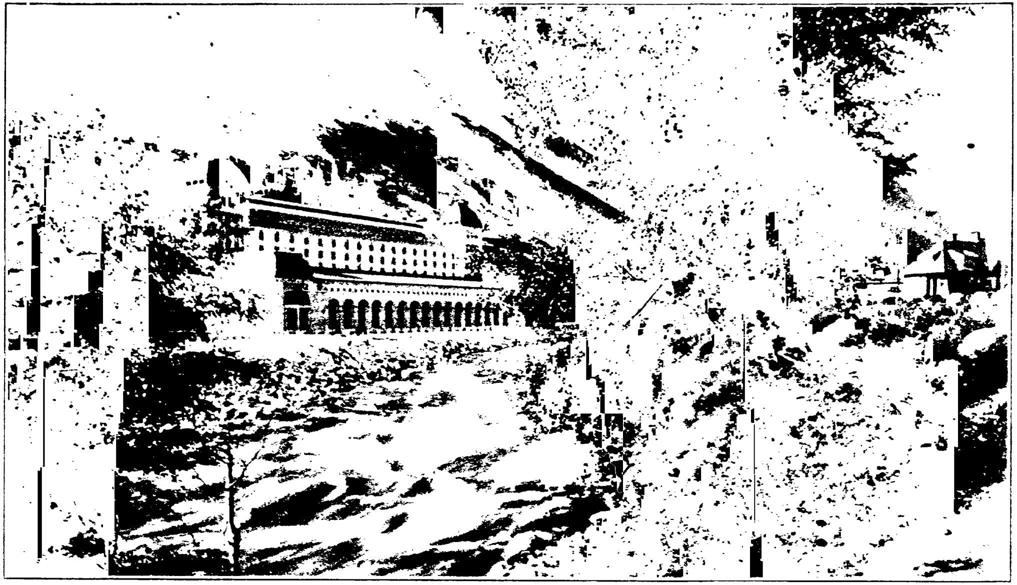
The Nitrogen Products Committee expressed the opinion that, with improved furnaces, the efficiency of the arc process could be increased by 10 to 15 per cent., and that with electrical energy at £3·75 per kilowatt-year the process might be operated economically. Recent very large increases in the price of coal, chiefly but not entirely owing to higher labour costs (p. 192), have made this figure of £3·75 impossible. In any case, since only 5 per cent. of the electrical energy is actually utilised in the arc process in performing electrochemical work (fixation of nitrogen), the remaining 95 per cent. appearing as sensible heat in the gas, which is largely wasted on cooling, it would appear highly undesirable to expend high-grade fuel on such a process, even if the economic difficulties could be overcome.

Incidental to the production of nitric acid, a large excess of heat is developed in the arc, which can be, and is in part, converted into steam, which is used to some extent for concentrating the weak nitric acid obtained in the absorption towers to the strong acid required for munition works. The excess of steam is so large that many other methods for its application have also been devised. The labour costs are low, since when once under way the operation goes on almost automatically. The formation of nitric acid is direct and involves only the nitrogen and oxygen of the air, and water, as raw materials; no complicated processes involving intermediate products are necessary, as is the case with the cyanamide process.

In spite of these manifest advantages, however, it appears to have been the general opinion of European engineers that even with the cheap power enjoyed by the Norwegian plants they might have had to discontinue their operations except for the stimulus given by the war. Even as it is, the Norsk Hydro Company, operating the arc plants at Notodden and Rjukan, were obliged to install large cyanamide ammonia plants in order that they might convert their nitric acid to ammonium nitrate, and thus render it transportable to markets where it was needed.

In a Report on "Nitrogen Fixation in the U.S.A.," issued in 1916, it is stated that "The cost of power used for the production of nitric acid in Norway is less than $5·00 per h.p.-year. The best estimates indicate that with power at $10 per h.p.-year the cost of finished strong nitric acid at the plant would be as cheap as by any other process now in operation. . . . The cost of installing the arc process is high,

PLATE XIV.



RJUKAN [illegible]I: POWER STATION (EXTERIOR).

To face p. 242.

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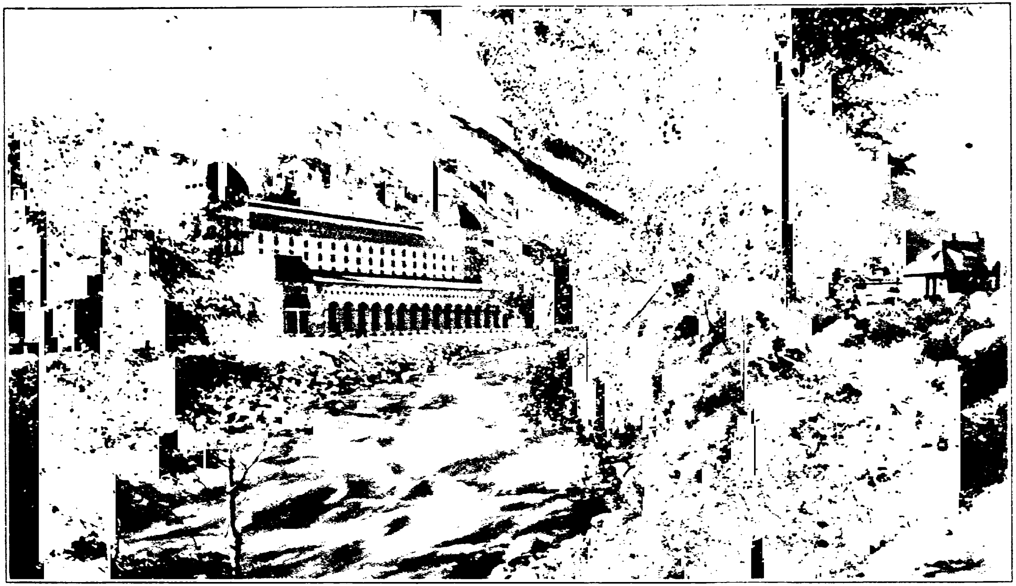

RJUKAN II.: POWER STATION (EXTERIOR).

To face p. 242

and it involves the use of an amount of power that is not available on the American continent within reach of the points where the nitric acid would have to be used."

Nitric acid is not economically transportable. As strong nitric acid it can be transported only if tank cars made of aluminium can be obtained, and aluminium is a metal that, for this purpose, has many disadvantages besides cost. The nitric acid might be transported mixed with sulphuric acid in iron tank cars, but this involves the erection of large sulphuric acid factories near to the nitric acid plant and a large addition in freight rates. Freight rates on such nitric acid as is transported are very high, and must always remain high, on account of the dangers involved.

Nitric acid does not readily lend itself to the production of fertiliser material, although it may be neutralised with lime to form calcium nitrate or with ammonia to form ammonium nitrate—both of which may be transported and either of which might be used as a fertiliser.

"The great difficulty that has faced the Norwegian plants from the beginning—namely, a market for their products—would in peace-times be a serious obstacle to the operation of a large arc plant in the United States. An arc plant at its best involves the use of 2·33 h.p.-years per ton of weak nitric acid. This means that a water-power development of at least 50,000 horse-power would be necessary for the peace requirements of the Government, and a development of 440,000 horse-power would be required for war purposes. These figures are minimum figures on the basis of the relatively high efficiency reached in Norway. No installation should be considered by the Government of less than 75,000 horse-power for peace requirements, or 550,000 horse-power for war requirements. If the arc process is to be used it would also be advisable to arrange for the production of explosives at the point where the arc plant was located. This would, of course, involve the transport of all other raw materials needed, such as benzol, toluol, alcohol, acetone, glycerine, sulphuric acid, cotton, and other materials too numerous to mention, to the plant, and the transport of the finished explosives therefrom to the place of consumption. As these materials are highly combustible and for the most part carry high freight rates, it has been found necessary the world over to locate the plants intended for the production of munitions near to the point where the munitions are likely to be consumed."

"An arc plant of sufficient size to meet the requirements of the Government in time of war would probably have to remain idle for the main part during times of peace, owing to the difficulty of disposing of the nitric acid that the plant would produce if in operation. On account of the large amount of power required and the consequent extent of the necessary plant and tower absorption capacity, the cost of installing an arc plant to meet the war-time requirements of the Government would be several times the total appropriation made for the purpose by Congress."

"ADVANTAGES.

"1. Cheapest cost of nitric acid* if power can be obtained at $10 per h.p.-year or less, and if the power is efficiently utilised in a large plant run continuously to capacity.

"2. Large amount of waste heat available for producing steam for the concentration of nitric acid and for other purposes.

"3. Free raw material.

"4. Direct production of nitric acid without intermediate products.

"5. Small amount of labour involved."

"DISADVANTAGES.

"1. Large amount of horse-power required per ton of nitric acid - at least 500,000 horse-power for the Government requirements.

"2. Greater dilution of nitric acid when first produced—30 to 35 per cent. acid as against 50 to 55 per cent. acid by other processes.

"3. Large cost of installation both for power and for plant —probably four times the present Government appropriation to meet the Government's war-time requirements.

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* This does not mean that it is the cheapest form of combined nitrogen for fertiliser purposes.

"4. Three-fourths of plant probably idle in time of peace, with consequent large idle investment involved.

"5. Non-transportability of the nitric acid produced.

"6. Difficulties of disposing of the nitric acid not needed for munitions."

The Norwegian Arc Industry.

The following details of the Norwegian arc industry are taken from a pamphlet, "Le Nitrate de Norvège, son emploi" (4th edition, Paris, 1913), issued by the Société norvégienne de l'azote, Christiania, Norway. The power employed at Notodden, the first factory erected using the Birkeland-Eyde process, is 55,000 h.p. The first large works at Rjukan uses 120,000 h.p., and the second Rjukan works uses 115,000 h.p. The group of works, using 300,000 h.p., is in operation night and day. In addition to these three Norwegian factories, there is a factory at Pierrefitte, in the French Pyrenees, and a similar works on the Spanish side, which is not actually in operation.

The main product, for agricultural purposes, is calcium nitrate. This is free from perchlorates and other injurious materials which are said to be present in some deliveries of Chile nitrate. It is sold in wooden barrels, holding 100 kilogrammes of nitrate, equivalent to 13 kilogrammes of fixed nitrogen. The contents are in the form of small grains, grey or brown in colour, ready for immediate application. The difference in colour depends solely on the different varieties of limestone used in the neutralisation of the nitric acid. The salt is odourless, and can replace Chile nitrate weight for weight for the same purposes. It is non-toxic, and is perfectly stable. It does not lose fixed nitrogen on keeping. The material can be kept indefinitely in the closed barrels. If part of the contents of the barrel are used, the rest may be kept without change by covering with a layer of dry ashes or plaster, and covering the barrel. The material is hygroscopic and rapidly attracts moisture. This is an objection, and the package should not be opened until the contents are to be used. In contact with the skin in wet weather, the salt may cause irritation. This may be avoided by washing in plenty of water. The salt is being made in a new form, free from fine powder, which very much reduces the danger of formation of dust.

The three Norwegian works are situated in the province of Telemarken. The Rjukan Fall has a height of 100 metres, and forms part of a series of cascades with a total fall of 560 metres. When the power is completely harnessed it will amount to 250,000 h.p. at Rjukan. The water is collected from the River Maana, and is dammed at Moesvand by a barrage. The water from the lake passes through a tunnel of 26 square metres cross-section and 4 kilometres long, cut in the rock, and ending in a huge water-house. . From this ten steel conduits, 2 metres in diameter, carry the water at the rate of 50 cubic metres per second to the groups of turbines in the electrical generating station. These conduits run down the side of a steep mountain to the power-house.

The power-house at Rjukan is 110 metres long and 20 metres wide. It contains ten turbines of 14,500 h.p. each. The electrical generators are coupled directly to the turbines.

The products are transported from Rjukan to Notodden, 47 kilometres by railway, which is electrified, 31 kilometres by steamers, on which the trucks are run directly, as in the steam ferry which plies between Germany and Sweden; and then arrive at Notodden. From this the materials are shipped to all parts of the world. The real port and warehouses are at Skien, near Notodden. Skien is about midway between Christiansand and Christiania.

A description of the works at Notodden and Rjukan is given in Thorpe's "Dictionary of Applied Chemistry," in the new article on the "Utilisation of Atmospheric Nitrogen." We shall here give a description of the newest works owned by the company, at Pierrefitte, in the French Pyrenees.

The Pierrefitte (Pyrenees) Works of the Société Norvégienne de l'Azote.

This works consumes an average of 8,000 kilowatts, and the production of nitric acid is about 4,000 metric tons of nitric acid (100 per cent.) per annum, the production being about 10 to 11 tons per day. The power is brought from an adjoining power-station owned by the Midi Railway Company, of France, and we gathered that the price paid was about 20s. per kilowatt-year. It is proposed to erect an independent station for the works.

The existing power-station was erected for the purpose of electrifying a considerable portion of the railway line in the vicinity. It was found, however, that the induction from the cables interfered very considerably with the telegraph service, and the scheme was prohibited by the State. Of the six generators installed, only one is used for electrifying the line between Lourdes and Cauterets. Another supplies power to the silico-manganese works at Pierrefitte, where an alloy is produced from manganese silicate imported from Spain. The remaining four generators are utilised by the Pierrefitte Arc Works. The water is taken from two lakes, one situated at Cauterets, at an altitude of 280 metres, and the other at Luz Saint-Sauveur, at an altitude of 140 metres. It is conducted through six flumes running down the Pic de Soulom, three to each lake, 3 feet and 4 feet in diameter from the places in the order stated. The high-pressure water passes to Pelton wheels, and the low pressure to turbines, in each case coupled directly to the alternators. The alternators operating on the high pressure are two by Westinghouse (utilised by the arc factory) and one by an Alsatian company of Belfort (utilised by the railway). The alternators operating on the low pressure are French Thomson-Houston machines, two used by the arc company and one by the silicon-manganese company. These Thomson-Houston machines are 3-phase 56-cycle, giving 9,500 volts at terminals and 152 ampères per phase (4.300 kilowatts). The particulars of the other types of machines were not taken, but were of much the same order. The railway current is transformed to 60,000 volts, which is stepped down to 10,000 volts at Lourdes.

The current is supplied to the arc works by underground cables direct at 10,000 volts, a portion being stepped down at the works by transformers to 380 volts, for lighting purposes. The choking coils in connection with the furnaces are water-cooled lead coils immersed in oil, and having an iron core. These are provided with an automatic thermometer, operating at 50° to 60°, at which temperature the current is cut off. The power losses in the choking coils were stated to be less than 1 per cent. The copper spirals without iron cores, as used at Notodden, have been abandoned.

The *furnace-room* contains four of the newest type of Birkeland-Eyde furnaces, about 10 feet in diameter, operating on single phase, up to 4,000 kilowatts. Three of these are in use and one is in reserve. The phases are interchangeable, one electrode being earthed. The furnaces are built of bricks and lined with a special Norwegian stone. There is a lenticular cavity containing the electrodes, one wall of which is perforated by holes for the admission of the air, which is sucked through the furnaces, and after passing through the arc leaves at the bottom of the furnace through a curved oval pipe about 2 feet in longest diameter and 1 foot in shortest diameter. This pipe is lined with resisting brick, and connects with the main flue carrying the gases to the boilers. This main is about 5 feet in diameter, and is lined with resisting brick 18 inches thick. The gases leave the furnaces at about 1,000° C.

The volume of air aspirated is about 5,000 cubic metres per furnace per hour, and the percentage of NO in the gas is 1·5 to 2 per cent. The air is *drawn* through the whole system by two fans in series placed after the alkali-absorption tower. Another fan is kept in reserve. It was found more economical to use two fans in series working at a lower speed than one fan working at a high speed. Each fan takes about 100 h.p. The drop in pressure inside the furnace was about 1½ inches of water.

The electrodes are ⊃-shaped copper tubes, water cooled, about 1 inch in diameter, separated by a distance of about ⅜ inch. The position of the electrodes can be regulated by screws outside the furnace. The arc is deflected by a large electromagnet placed in a cavity on the side of the furnace through which the air is drawn. Current for these magnets is obtained from a rotary converter. The average life of an electrode is from three to four weeks. The furnaces emit a deep roaring note, which, however, is not unpleasant.

The gases in the mains leading from the furnaces enter at about 980° C. into two Babcock boilers, each having about

PLATE XV.

[illegible] POWER STATION. INTERIOR.

300 square metres of heating surface, and provided with superheaters and economisers. A considerable amount of steam is blown off to waste after all requirements are satisfied. The water from supply is very hard and is softened before use. After passing through the boiler fireboxes, the gases leave at about 250° C. to the coolers.

The *coolers* are placed in the open air, and are four in number, consisting of a battery of iron tubes contained in a vertical tank through which water flows.

The gases then pass to an oxidation tower, which is constructed of sheet iron, and is of sufficient volume to give one minute's contact for the gases. The temperature of exit from this tower is 50° C.

The drop in pressure in the coolers is about 40 mm. of water, and in the oxidation tower is 5 mm.

The gases then enter the *absorption towers*, which are four in number, constructed of slabs of Norwegian granite, clamped by sixty-one iron bands. Attempts were made to use the local granite, but this was found unsuitable, owing to a tendency to disintegrate. The towers are ten-sided in horizontal section; 26·925 metres high inside and 7·3 metres external diameter (uniform). The thickness varies from 350 mm. at the bottom to about one-third the way up the tower, and then diminishes in steps, 300, 250, and 200 mm. They are mounted on concrete piers, all joints being accessible and visible. There was no noticeable leakage. The packing consists of pieces of Norwegian quartz about the size of a walnut, the local material being again unsuitable, owing to its iron content. The towers are completely packed, and there is very little free space.

The gases enter at the bottom of the first tower, and alternately at the top and bottom of the successive towers.

The acid is circulated in each tower by one compressed-air montejus, which is constructed of iron lined with acid-resisting stoneware, and having a capacity of 400 litres. The circulation is intermittent, the montejus being emptied every two to three minutes. There was one 4-inch stoneware pipe to each tower with "Almagam" rubber joints, for circulation in that tower, and one similar pipe for transferring acid from the next later tower in the series. The circulation works out at about 10,000 litres of acid per hour. It is proposed, if possible, to replace the montejus by centrifugal Tantiron pumps. The dome of the tower is in sections, jointed together with blue asbestos covered with tar.

The acid flows from each tower into a large granite tank, with an aluminium cover, from which it is taken to the montejus.

The strength of acid withdrawn from the first tower for use is about 30 per cent., but this can be raised to 52 per cent. by slower circulation. The strengths of acid in the other towers are usually 20 per cent., 10 per cent., and 5 per cent. respectively. The time of passage of the gas in each tower is about one minute.

After leaving the water-absorption towers the gases enter an alkali-absorption tower made of sheet iron, and about the same size as the water towers, and also packed with quartz. Through this is passed a solution of sodium carbonate. The sodium carbonate contains about 2 per cent. of caustic soda, and is converted to sodium nitrite.

The strength of sodium nitrite solution withdrawn from the tower may be as high as 30 per cent.

The drop in pressure through the absorption system is as follows:

1st water tower	..	..	125 mm. water.
2nd ,,	..	..	150 ,, ,,
3rd ,,	..	..	100 ,, ,,
4th ,,	..	..	150 ,, ,,
Alkali tower	..	..	130 ,, ,,

The time of passage of the gases through the whole system is five to six minutes. The gases then pass to the fans and the exit to the open air. This exit, when we visited the works, was quite visibly red. This was on a very wet day, but it was stated that on a very dry day the effluent was barely visible.

It was stated that the over-all absorption amounted to 96 to 97 per cent. of the oxidised nitrogen leaving the furnace, 90 per cent. being recovered as nitric acid and the remainder as sodium nitrate. (The sodium nitrate figure refers to the treatment of the product of absorption in the alkali tower with dilute nitric acid, followed by passage of the evolved oxides of nitrogen through the absorption system.)

The *yield* reckoned on nitric acid and sodium nitrate made, compared with power entering the factory and used for all purposes, was stated to be 550 kilogrammes HNO_3 per kilowatt-year.

If this is referred to power measured at the switchboard and used solely for the operation of the furnaces, the yield is increased to about 560 kilogrammes HNO_3 per kilowatt-year. This works out to about 63 grammes HNO_3 per kilowatt-hour (8,760 hours per year).

Concentration.—The 30 per cent. acid from the towers is pumped to a reservoir, from which it descends four granite towers 10 feet in diameter and about 50 feet nigh, lined with acid-resisting brick and packed with broken quartz. Here it meets steam from weak acid concentrating plant, receiving a preliminary concentration. This acid also receives a preheating before entering the towers by means of waste steam from another section of the plant.

The concentrater proper consists of four steam-jacketed tubes of Tantiron, connected with a bell shaped catch all; steam at 8 kilogrammes per square centimetre pressure is passed through the jackets, and evaporation is effected under ordinary pressure. Each tower is connected with a battery of four of these concentraters—*i.e.*, sixteen steam jacketed tubes in all. In this apparatus the acid is brought up to 60 per cent. strength. (When seen by us this plant was concentrating sodium nitrate solution.) This 60 per cent. acid is collected in four granite reservoirs, and is pumped to a single reservoir placed at the top of the building, whence it flows into two granite towers (octagonal) about 8 feet in diameter and 30 feet high (with one as reserve). Into the same tower is run concentrated sulphuric acid (80 per cent.) from a tank alongside the 60 per cent. nitric-acid tank. Nitric acid of 96 to 97 per cent. strength is distilled over, and is condensed in aluminium S pipes placed between the two towers.

This acid is then sent down a small granite tower through which a current of compressed air is passed to remove the oxides of nitrogen. The diluted sulphuric acid (60 to 65 per cent.) is reconcentrated in a plant similar to that used for making 60 per cent. nitric acid, except that it is worked under vacuum. The vacuum is maintained by a vertical fall pipe and condensing jet.

Sodium nitrate is made in two ways:

(1) Treating tower acid with sodium carbonate, the CO_2 being removed, together with some oxides of nitrogen, by fans.

(2) Treating nitrite solution from alkali tower with tower acid in a granite tank with an aluminium cover, the evolved oxides of nitrogen being aspirated back into the absorption system.

The *sodium nitrite* is also concentrated in an apparatus similar to that described, the final operation being effected in five pans about 5 feet by 20 feet by 2 feet, heated with steam coils. Both salts are dried in centrifuges and bagged.

Ammonium nitrate is made by neutralising tower acid with ammonia solution sent in iron drums from Bassens, each drum holding about 30 gallons. The solution is concentrated in a Tantiron apparatus, being kept faintly alkaline, and the salt is crystallised in an aluminium rotor about 3 feet in diameter and 20 feet long, which is cooled by a shower of water on the outside.

A mineral called "steatite" from Norway is used as an acid and heat resistant and an insulator. It is said to have the same composition as talc, but is harder.

On the occasion of our visit attempts were being made to manufacture calcium nitrate from local limestone, said to be of 95 per cent. purity.

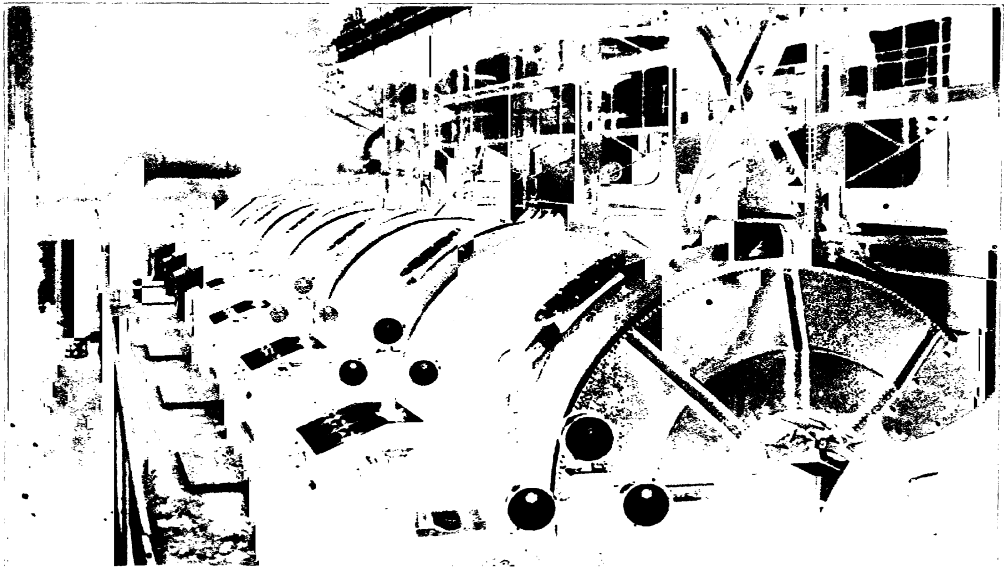
The absorption in the towers was very little affected by the seasonal temperature extremes at Pierrefitte, and consequently great difficulties would not be met with in this direction in a warm climate. A 10-metre fall of water of large capacity would be of practical utility.

This works at Pierrefitte was erected in six months, the French official estimate being two years.

ESTIMATE OF PRODUCTION COSTS.

	£	s.	d.	
Cost of power estimated at 20s. per kilowatt-year, therefore cost of power per 1 ton HNO_3 ..	2	0	0	(about).
Labour charges (say 20 men at 5s. per day) ..	0	10	0	per ton HNO_3.
Staff charges, etc.	0	10	0	,, ,,
Concentration costs	2	0	0	,, ,,
Extras, etc.	1	0	0	,, ,,
Total ..	£6	0	0	,, ,,

PLATE XVI.



BIRKELAND-EYDE FURNACES, SAAHEIM

(Schönherr Furnaces on extreme left)

The strong acid is sent out in strong earthenware bottles, holding about 30 gallons; aluminium vessels had shown themselves very unsatisfactory.

The "Nitrum" Arc Process.

In a recent improvement of the arc process a mixture of equal volumes of nitrogen and oxygen ("enriched air") is circulated through the arc furnace, coolers, and absorption plant as a closed cycle. The percentage conversion in the arc would be somewhat higher in this case, since the oxygen and nitrogen are in the exact proportions in which they combine together to form nitric oxide, and the chance of collision of an oxygen and nitrogen molecule at the high temperature of the arc is therefore higher than when an excess of nitrogen is present. The chief gain, however, would seem to be in the much enhanced rate of oxidation and absorption of the gases in presence of an excess of oxygen, so that the very costly granite towers used in the treatment of the gases for the production of dilute nitric acid are greatly reduced in size. It would probably be even better to use an excess of oxygen over the equal ratio $N_2 : O_2$, since, although the rate of combination of the gases in the arc would be again somewhat reduced, this would be far more than compensated by the rapidity of absorption of the resulting gases. It must be emphasised that, next to the cost of generation of energy, the capital cost of the towers and absorption plant is the main factor in the economics of the arc process. A few tenths of a per cent., or even one or two units per cent., in the efficiency of the furnace itself is a small matter in comparison with the cost of the treatment of the gases after they have left the furnace.

The process utilises the electric arc for the oxidation of atmospheric nitrogen, but differs from established practice in one or two important respects. Firstly, the gases supplied to the furnaces are enriched with oxygen to a content of 50 per cent.; secondly, the gases circulate in a closed system, so that only so much oxygen has to be supplied as is actually used in the formation of the final products; thirdly, the absorption system is said to be of special design, and to be of much smaller dimensions than usual, owing to the high oxygen content of the gases; and fourthly, cooling is applied to the gases and liquid circulating in the absorption system.

The gases supplied to the furnaces are dried by refrigeration before being acted upon by the electric arc. The nitrogen is obtained from the air, and is enriched with oxygen to maintain an average concentration of 50 per cent. The gases are circulated throughout the plant in an enclosed system, and only sufficient fresh oxygen is added to replace that consumed in the formation of nitrogen dioxide and nitric acid. A portion of the gas, however, is vented from time to time to prevent the accumulation of argon, and the oxygen content is allowed to rise to about 52 per cent. About 1 cubic metre of mixed gas is supplied per hour for each kilowatt capacity of the individual furnaces. This rate of flow is less than average practice on account of the enrichment. The gas leaving the furnaces is stated to be at a temperature of some 1,500° C. (measured by Seger cones), and contains 2·5 to 3 per cent. of nitric oxide. The arrangements for cooling the gases are secret, but the temperature is kept in the region of 0° C. in all the absorption towers. The steam raised by the heat contained in the gases leaving the furnaces is sufficient for evaporation purposes, for generating power for the refrigeration and oxygen plants, and for the auxiliary services.

Oxygen Plant.—It is said to be most economical to make commercial oxygen of 78 per cent. purity; it would not pay to make pure nitrogen as well for cyanamide. A Linde unit makes about 1,000 cubic metres of oxygen per hour at a cost of about 3 centimes per cubic metre; the working cost is about 1 centime per cubic metre. The cost of the oxygen plant amounts to about 10 per cent. of the whole.

Electric Equipment.—The process requires inductances of considerable magnitude in series with the furnaces, and three arcs are put together to obtain the flame. The power factor of the furnaces is raised from 0·5 to 0·7 by the use of synchronous motors, and these power-factor correctors have to be of considerable capacity. The inductance costs about three times as much as the furnace, and an expensive step-up transformer is necessary for each 3-phase unit.

The Furnaces.—Special 3-phase furnaces are used, which are said to be equally efficient over the range of capacity from 400 to 3,000 kilowatts. No magnets are used. Three thousand kilowatt furnaces are actually in operation, and no difficulty is anticipated in the working of larger units—say of 4,000 to 5,000 kilowatts capacity. The power factor of the furnaces is 0·5, and about 1 in 4 is kept in reserve. Overheating is avoided by the method of circulation of the gases, and there has been no trouble with the refractory material, which consists of Dinas rock.

The furnaces are easy to start up and to stop, and it even pays to operate for one hour only.

The Electrodes are formed of special electric steel and are water-cooled, the iron not being found detrimental to the process. Each electrode will last seventy-two working hours, and can be changed in six hours. Work on the electrodes can be started within thirty minutes of shutting down, the furnace being cooled by a blast of cold air

Absorption.—Water absorption alone is used, no alkali towers being necessary. The absorption towers are of secret and special design, in which 95 per cent. of the fixed nitrogen is said to be recovered. Great reduction in gross space is said to be obtained, due to—

(i.) The enrichment of the gases with oxygen.
(ii.) The cooling of the gases and the circulating liquid.
(iii.) Special secret devices (!).

The gases and circulating liquid are cooled to the neighbourhood of 0° C. in all the towers, and it is said that a 250-h.p. refrigerating machine will account for 1 million cal. The cooling system is said to be independent of extremes in external temperature. The cost of the absorption system amounts to about 10 per cent. of the whole.

Products.—Sixty-two per cent. nitric acid is obtained from the towers. A similar system without the use of oxygen or cooling would give 45 per cent. acid, and only 85 per cent. of the fixed nitrogen would be recovered. The process is capable of making a dry nitrate of lime containing 16 per cent. of nitrogen as a maximum, and the product is said to be less hygroscopic than usual. One kilogramme of nitrogen as final packed product is said to require the expenditure of 16·5 to 17 kilowatt-hours. Thin iron drums may be used for packing.

Yield.—This is said to amount to 70 to 75 grammes calculated as pure HNO_3 obtained as 62 per cent. acid per kilowatt-hour, the energy being measured at the furnaces.

Existing Installations.—The process described is worked by the "Nitrum Company" of Switzerland.

1. *Bodio, Switzerland.*—The factory has been operating since 1910, and utilises 6,000 kilowatts for the manufacture of nitric acid, sodium nitrate, and sodium nitrite. For making nitrate of lime the nitric acid must be diluted to 50 to 55 per cent. strength. The loss in neutralisation is said to be negligible. Experiments have also been conducted on liquefaction processes for the removal of nitrogen dioxide from the gases. The liquid is stored in metal drums, sometimes of aluminium, holding as much as 80 tons of the liquid. Transport is effected in tank wagons holding 15,000 kilogrammes. The necessary refrigeration is effected by means of the cold nitrogen from the liquid-air plant, and it is easy to obtain 70 to 75 per cent. nitric acid directly from the liquid, when pure oxygen is used in conjunction. This factory was destroyed by explosion in the summer of 1921.

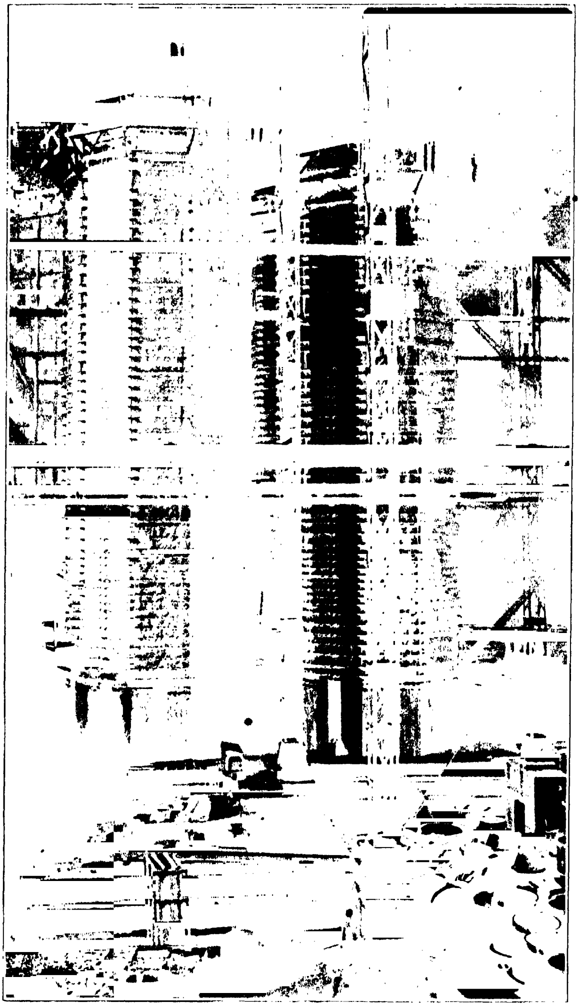
2. *Lauffenburg, Germany.*—A licence was granted in 1916 for a factory utilising 15,000 kilowatts. Power is generated at 6,000 volts, and transformers raise this to 12,000 to 18,000 volts. Three thousand kilowatt furnaces are in operation, and the power is used for fixation purposes during the night.

This factory works more economically than the one at Bodio, 1 kilogramme of nitrogen fixed as 62 per cent. nitric acid costing 1 franc 20 centimes, with power at just under 1 centime per kilowatt-hour.

Seventy grammes HNO_3 are obtained per kilowatt-hour, with the energy measured at the furnaces or switchboard. The nitric acid is said to be cheaper than that made by the Haber process.

3. *Schornewitz, near Merseburg.*—A 60,000-kilowatt installation was erected here, but was blown up. The explosions in factories (1) and (3) seem to have been caused by leakage of

PLATE XVII.



NITRIC ACID ABSORPTION TOWERS.

To face p. 266.

combustible liquids, used for refrigeration, into the nitrogen dioxide produced by the process.

Economics.—The difference in cost, with and without the use of oxygen, amounts to about 70 centimes per kilogramme of nitrogen at Bodio (2·5 to 3·2 francs). With the same cost, about 20 per cent. more nitrogen is fixed by one method than by the other. The more expensive the energy, the more it pays to use oxygen.

The Schloesing Process.

An alternative method of absorption of the arc furnace gases has been proposed by Professor A. T. Schloesing, of Paris, and trials were made at the works at Notodden. Although the process is not at present in use, the information we have received from different sources leads us to conclude that the method proved successful in so far as the absorption was concerned. The process consists in the prolonged action of the somewhat cooled arc-furnace gas on specially prepared quicklime, whereby a basic nitrate of lime, suitable for use as a fertiliser, is ultimately obtained. The objections to the process for Norwegian works are that coal is required for the preparation of the lime, and that the operating costs are high.

It appears that in the plant which operated at Notodden six chambers were at work, the temperature in which reached 340° to 350° C. This temperature is kept up by the heat contained in the entering gases, and also by that evolved during the reaction. There is plenty of heat to spare in a large installation.

It was stated that the quantity of oxides of nitrogen in the exit gases was negligible, and we have seen routine analysis sheets from Notodden, covering a period of several weeks, which showed "100 per cent. absorption."

The time of contact of the gases throughout the plant was two minutes, as against eight minutes in water-absorption towers. In a small plant the temperature of exit of the gases was 175° C.

Professor Schloesing has emphasised the importance of employing dry gases, and for this reason the air is dried by passage through a tower down which sulphuric acid flows before entering the arc furnace. He stated that it was possible to get up to 15 to 17 per cent. of nitrogen in the absorption product (pure $Ca(NO_3)_2$ requires 17·1 per cent. N), but the usual figure obtained under working conditions was in the neighbourhood of 14 per cent. of nitrogen.

A very light limestone is necessary for good absorption, and it was stated that the material from Dover, Boulogne, or Etaples was very suitable. We have inspected samples of the Etaples variety, which seemed a material of very suitable quality.

The preparation of the lime requires special attention. The lime prepared by burning the native material at a low temperature is slaked and dehydrated, the second calcination being performed at a low temperature. A lime which has been over-calcined will regain its activity if reslaked and properly dehydrated. The material is pressed into pastille form, and such pastilles are very active towards water, disintegrating and hydrating almost explosively in contact with that liquid.

The gases leave the arc furnace at 800° C. and enter the absorption system at about 100° C., and this drop in temperature is used to dehydrate the lime. No oxidation chambers are fixed between the absorption chambers, since at the temperature used nitrogen peroxide does not exist.

Professor Schloesing is emphatic that there was no loss of nitrogen in its elementary form during the progress of the reaction which embodies the principle of his process. Such a loss has been proved conclusively in our experiments under the conditions with which we worked namely, with the nitrous gases in such concentration as is obtained from an ammonia oxidation converter though we support his contention that the product could, under certain conditions, such as the length of time the absorption material was exposed to the gases, be obtained free from nitrite. The loss of nitrogen had also been observed by M. Oswald. Professor Schloesing states that he had made similar experiments. He found no loss as elementary nitrogen, but the product contained nitrite, because the gas was not circulated. At the same time he admitted the difficulty of analysis, and of obtaining an accurate figure for the total nitrogen in the system.

Later (unpublished) experiments by one of the authors (J. R. P.) and Mr. E. Whitworth have confirmed Professor Schloesing's results in so far as they showed that lime prepared from Dover chalk in the special manner described absorbed dilute nitrous gases (1 per cent. NO) with formation of nitrate and without liberation of nitrogen. With *ordinary* lime from the same source liberation of nitrogen was again observed.

Economics of the Arc Process.

The capital cost of the factory for the arc process is high in comparison with that in most other nitrogen-fixation processes. The Nitrogen Processes Committee estimate the total capital outlay (pre-war) for a large-scale factory for the production of *concentrated* nitric acid to be £178·54 per metric ton of nitrogen fixed per annum, or nearly twice the pre-war market value of the annual production. Of this sum, the arc furnace, absorption, and concentrating plant would amount to about £92, and the steam-power section to about £86. They also consider the possible cost of water power plant on a site in the United Kingdom which is regarded as suitable for hydro-electric development. Continuous power of over 28,000 kilowatts is estimated to be available, the estimated cost of development on the basis of a 50 per cent. increase on pre-war contract prices being £61 per effective kilowatt, inclusive of hydraulic works, water rights, land, power-station, electrical equipment, and spare plant. The estimated working costs, inclusive of repairs, maintenance, and depreciation of power-house plant and other works at 7·5 per cent. per annum, amortisation and occasional repairs of hydraulic works at 1 per cent., and interest on capital at the rate of 4·5 per cent. per annum, amount to £3·93 per kilowatt-year of 8,760 hours. On this basis comparison is made with a figure of £3·8 per kilowatt-year for electrical power derived from a large coal-fired steam plant, but as the latter figure is based on coal at a much lower price (7s. 6d. per ton) than is now possible, it is evident that the hydro-electric installation would have the advantage if the increase of 50 per cent. over pre-war costs is adequate. The Committee, in fact, expressed the opinion that " it is improbable that this low figure (£3·93 for hydro-electric power) will be obtainable even by the best coal-fired power-station practice when regard is had to the future cost of coal."

After examining various possible methods of utilising by-products (*e.g.*, by high-temperature carbonisation, or by the use of gas producers), the Committee came very definitely to the conclusion that, *of processes which had actually been operated under large-scale conditions*, direct coal-fired steam turbo-generator plant was the one to be preferred if low cost of power were aimed at. Under such conditions, for a power station having a maximum load of 100,000 kilowatts and an annual load factor of 100 per cent., the estimated cost upon a *pre-war* basis, with coal at 7s. 6d. per ton, would be £3 8s. per kilowatt-year. This figure requires modification for increased labour and fuel charges. The estimate given by the Committee is as given on p. 261.

Since 8·41 kilowatt-years are required per metric ton of nitrogen fixed by the arc process, the capital outlay for the steam-power station would amount to 8·41 × £10·26 = £86·29 (pre-war), as stated on p. 261.

The above cost may be compared with the capital costs of water-power development in known cases:

(1) Norway (falls of great height; easy storage), £6 to £8 lowest; moderate, £14 to £15.

(2) United States average (£23 to £30), £26.

(3) Kinlochleven (Scotland), £31.

Whilst improvements in design and construction may be expected to diminish the capital cost of steam-power plant, the opposite may be expected of water-power as the most favourable sites become developed.

The conversion of the above items (*a*) to (*h*) of capital cost to post-war conditions may easily be effected by adding on the requisite percentage in each case. The greatly increased costs under items (*b*), (*d*), and (*e*) will probably nearly double the final figure.

The cost of generation of electrical energy by steam power is largely controlled by the price of coal. The cost of fuel amounted, on the pre-war estimate, to 63 per cent. of the total costs.

DETAILS OF STATION.

Plant installed at normal rating, 125,000 kilowatts.
Maximum effective load at normal rating, 100,000 kilowatts.

30 boilers installed	1,500,000 pounds steam per hour.
24 boilers working	1,200,000 „ „
Size of turbo-alternators	25,000 kilowatts each.

PRE-WAR CAPITAL COST OF 100,000-KILOWATTS STATION.

Items.	*Total.*	*Per Kilowatt Installed.*	*Per Kilowatt Maximum.*
	£	£	£
(*a*) Land for complete station	20,000	0·16	0·200
(*b*) Buildings and foundations, coal silos and transporters, railway sidings, roads, etc.	187,500	1·50	1·875
(*c*) Coal and ash handling plant	30,000	0·24	0·300
(*d*) Boilers, superheaters, reheaters, feed heaters, mechanical stokers, induced-draught plant, chimneys, etc.	225,000	1·80	2·250
(*e*) Turbo-alternators and exciters, surface condensers, air pumps, and auxiliaries	312,500	2·50	3·125
(*f*) Steam and water piping, circulating and feed pumps, air pumps, strainers, etc.	75,000	0·60	0·750
(*g*) High and low tension switchgear, reactances, etc.	100,000	0·80	1·000
(*h*) Engineering supervision, inspection, contingencies, etc.	76,000	0·60	0·760
Total ..	£1,026,000	£8·20	£10·260

The annual working expenses, under pre-war conditions, of a coal-fired power-station of 100,000 kilowatts maximum demand operating at load factors of 95, 97·5, and 100 per cent. respectively, are estimated as in the following table by the Nitrogen Products Committee on the following bases:

Maximum load	100,000 kilowatts.
Calorific value of coal as fired*	12,500 B.Th.U. per pound.
Thermal efficiency of boilers with superheaters and economisers	80 per cent.
B.Th.U. per kilowatt-hour output	20,000
Cost of coal	7s. 6d. per ton.

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* The *calorific value* in British Thermal Units (B.Th.U.) represents the number of pounds of water raised 1° F. in temperature by the heat given out in the combustion of 1 pound of the fuel.

PRE-WAR COST OF GENERATION AT 100,000 KILOWATT STATION.

Items.	(A) *Load Factor* = 95 *per Cent.* *Kilowatt-Year* = 8,322 *Hours.* *Units* = 832,200,000			(B) *Load Factor* = 97·5 *per Cent.* *Kilowatt-Year* = 8,541 *Hours.* *Units* = 854,100,000			(C) *Load Factor* = 100 *per Cent.* *Kilowatt-Year* = 8,760 *Hours.* *Units* = 876,000,000		
	Annual Expenses.	*Per Unit.*	*Per Kilowatt-Year.*	*Annual Expenses.*	*Per Unit.*	*Per Kilowatt-Year.*	*Annual Expenses.*	*Per Unit.*	*Per Kilowatt-Year.*
	£	*d.*	£	£	*d.*	£	£	*d.*	£
(*a*) Salaries and wages	14,000	0·00403	0·140	14,000	0·00393	0·140	14,000	0·00383	0·140
(*b*) Oil, stores, and sundries ..	10,000	0·00288	0·100	10,000	0·00281	0·100	10,000	0·00274	0·100
(*c*) Repairs and maintenance ..	30,000	0·00864	0·300	30,000	0·00843	0·300	30,000	0·00822	0·300
(*d*) Coal—									
(A) 594,430 tons	222,912	0·06429	2·229	—	—	—	—	—	—
(B) 610,070 tons	—	—	—	228,776	0·06429	2·288	—	—	—
(C) 625,710 tons	—	—	—	—	—	—	234,641	0·06429	2·346
(*e*) Capital charges	91,327	0·02633	0·913	91,327	0·02566	0·913	91,327	0·02502	0·913
Totals	368,239	0·10617	3·682	374,103	0·10512	3·741	379,968	0·10410	3·799
Or, say	368,500	0·1062	3·685	374,500	0·1052	3·745	380,000	0·1041	3·800

The annual capital charges are made up as follows:

(i.) 4½ per cent. interest on capital taken as a fair average over a period of years.
(ii.) 2½ per cent. depreciation on buildings, etc. (item *b*), and on the corresponding proportion of contingencies and engineering fees.
(iii.) 5 per cent. depreciation on the remaining capital (items *c* to *g*), and on the corresponding proportion of contingencies and engineering fees.

No depreciation has been taken on land and its proportion of contingencies and engineering fees. No sums are included for insurance, imperial taxes, or local rates.

The effect of the price of coal has been considered by the Committee in a table. In this, coal at 5s. and 10s. per ton has been included, but since the cheapest post-war coal will probably be 20s. to 25s., these figures have been added for comparison.

Load Factor.	*Cost of Energy in £ per Kilowatt-Year with Coal at per Ton—*				
	5s.	7s. 6d.	10s.	20s.	25s.
	£	£	£	£	£
(A). 95 per cent. (8,322 hours)	2·942	3·685	4·428	7·400	8·890
(B) 97·5 ,, (8,541 ,,)	2·982	3·745	4·508	7·559	9·084
(C) 100 ,, (8,760 ,,)	3·018	3·800	4·582	7·710	9·274

The Committee emphasise that it is possible to obtain electrical energy from coal at a cost comparable with that of water power only by resorting to steam power plant of large size: a minimum scale of 30,000 kilowatts is given for the manufacture of cyanamide.

They further criticise the proposal, often made, to burn the coal at the colliery, or even at the pit's mouth, in order to reduce transport charges, by pointing out that, for a 100,000-kilowatt station with a load factor of 95 per cent., some 136,000,000 gallons of cooling water per day would be required, and if cooling towers were employed as an alternative to a natural supply of circulating water, a daily supply of 2,720,000 gallons would be required to make up losses by evaporation, and in this case, owing to the lower vacuum consequent on the higher temperature of the cooling water, an additional 35,600 tons of coal would be used per annum. A waterside station would, therefore, seem imperative, the coal being carried from the pit to the station. It must not be lost sight of that important coalfields (*e.g.*, Cumberland and Yorkshire) are situated near the sea.

Before proceeding to a more detailed account of the actual nitrogen-fixation works, a table giving the relative power requirements of the three important processes may be given:

Power Requirements of Nitrogen-Fixation Process.

Fixation Process.	*Kilowatt-Hours per Kilogramme Nitrogen Fixed.*	*Kilowatt-Years per Metric Ton Nitrogen Fixed (8,760 Hours).*	*H.P. Years per Long Ton Nitrogen Fixed.*
Arc (exclusive of steam-raising value of furnace gas)	73·7	8·41	11·45
Cyanamide	16·5 to 19·5	2·03 to 2·37	2·76 to 3·23
Haber (assuming power supplied electrically) ..	3·6	0·435	0·592

With respect to the arc process, the Nitrogen Products Committee make the following remarks: "This synthetic process involves the direct combination of atmospheric nitrogen and oxygen by the heat of the electric arc, and the absorption of the resulting oxides of nitrogen in water and subsequently in alkali. The primary product of the absorption is dilute nitric acid of 30 to 40 per cent. strength, but about 15 per cent. of the total nitrogen fixed is absorbed in the alkali towers, and can be recovered as sodium nitrate. The dilute acid can be concentrated further if desired, or neutralised with an appropriate base for the production of solid nitrate salts, such as nitrate of lime or ammonium nitrate. The process is simple and continuous in operation, air and water being the principal raw materials.

"The most striking characteristics of the process as hitherto developed in countries where cheap water power is available are—

> "(*a*) The large power requirements per unit of nitrogen fixed;
>
> "(*b*) The low electrochemical efficiency; and
>
> "(*c*) The extensive and costly character of the absorption plant."

They point out that the arc process, if operated on a scale of 15,000 to 20,000 kilowatts, could produce *concentrated* nitric acid at a lower cost than the retort process from Chile nitrate at £10 10s. per ton, as long as the cost of electrical energy does not exceed £9 per kilowatt-year.

The amounts of nitrogen fixed per annum by a continuous power supply of 100,000 kilowatts are as follows:

(*a*) *Arc Process*: 11,890 metric tons in the form of 53,500 metric tons of nitric acid (as 100 per cent. HNO_3).

(*b*) *Cyanamide Process*: 50,760 tons, in the form of over 260,000 metric tons of raw cyanamide (19·5 per cent. N).

(*c*) *Haber Process*: 230,000 metric tons, in the form of 280,000 metric tons anhydrous ammonia (NH_3), or 1,100,000 metric tons of ammonium sulphate (100 per cent. $(NH_4)_2SO_4$).

The by-product nitrogen lost by the combustion of the coal in direct firing would amount to as much as 10 to 100 per cent. of the capacity of an arc-fixation plant, and 2 to 24 per cent. of that capable of being fixed by a cyanamide plant. When the potential value of these lost by-products is taken into account, it does not necessarily follow that direct coal-firing is the cheapest method of obtaining power from coal. If *existing* methods of utilising coal for power are considered, however, and full value credited to by-products, it is still found that direct firing is most economical.

The question of using gas engines for power generation was considered by the Committee. They decided that at the present time it would be entirely impracticable and uneconomical to employ gas engines for power-stations of the size necessary for the competitive operation of nitrogen-fixation processes under British conditions. For small blocks of power the position is much more favourable, both as regards capital cost and working costs, the latter being as low as, or even lower than, the corresponding costs for steam-power plants. The largest gas-engine electric units installed commercially in this country have a capacity of less than 4,000 kilowatts. The utilisation of peat by gasification is even more problematical. The principal difficulty to be overcome is the excavating and drying of sufficiently large quantities of peat all the year round under varying climatic conditions and at a cost which will permit of the economic use of the resulting low-grade fuel. The failure of the "wet-carbonising" process, which was to effect this, will be fresh in the minds of most readers.

The complete gasification of coal in a single stage in existing types of recovery producers, if applied to power production on a large scale, would offer little prospect of competing financially with direct coal-firing, because of the prohibitive price of coal. Such a process would not permit of the recovery of the oil and tar products to a satisfactory extent, although it would give a high yield of ammonia.

High-temperature carbonisation, in gas-retorts or coke ovens, as a stage in the production of power would be handicapped by capital and operating costs, and offers no prospect of competing upon a commercial basis with direct coal-firing. The process also compares unfavourably with other by-product recovery processes from the standpoint of the potential yield of nitrogenous and other by-products. A daily output of from 400 to 500 million cubic feet of gas, or from five to six times the maximum daily output of the largest individual gasworks in the world, is also to be reckoned with in any scheme for the gasification of fuel as a preliminary to its utilisation in a nitrogen-fixation works of economic size.

The cost of producing nitric acid, or nitrates, by the arc process includes, in addition to the cost of power, charges for plant and labour, and other materials such as limestone, soda ash, or ammonia liquor if nitrates are manufactured.

On a pre-war basis, the Nitrogen Products Committee estimate that with electrical energy at £3·75 per kilowatt-year the cost of production of *concentrated* nitric acid by the arc process would amount to £11·5 per metric ton of HNO_3 (100 per cent.), or about *half* the cost of the acid made by the retort process from Chile nitre (£22·3 per metric ton HNO_3). Every additional £1 in the cost of energy per kilowatt-year increases the cost of production of the acid by £1·87 per metric ton, since 1·87 kilowatt-years of energy are required per metric ton of acid made.

The pre-war capital cost of a large arc plant under Norwegian conditions was stated to be £8·294 per kilowatt installed, or since 8·41 kilowatt-years are required per metric ton of nitrogen fixed, the capital cost was £8·294 × 8·41 = £69·75 per metric ton of nitrogen fixed per annum in the form of *dilute* nitric acid. The estimated capital cost of a concentrating plant for the conversion of this dilute acid into concentrated acid is estimated as £22·50 per metric ton of nitrogen.

The cost of the power plant of 100,000 kilowatt capacity, steam power, amounts on a pre-war basis to £10·26 per kilowatt; hence the cost per metric ton of nitrogen fixed will be £10·26 × 8·41 = £86·29.

The total capital cost of an arc factory operated by steam power producing concentrated nitric acid would therefore be, per metric ton of combined nitrogen, £69·75 + £86·29 + £22·50 = £178·54.

The production cost of *dilute* acid, exclusive of cost of energy and of interest on capital, is taken by the Nitrogen Products Committee as £2·5 per metric ton nitric acid (as 100 per cent. HNO_3) or £11·25 per metric ton of combined nitrogen. This figure includes labour, repairs, general charges, amortisation of the arc furnace installation at an equated value of 8 per cent., and materials (exclusive of soda for the alkaline-absorption towers).

The cost of concentrating the dilute acid to produce concentrated nitric acid is taken as £2 per metric ton of nitric acid (100 per cent. NHO_3) or £9 per metric ton of combined nitrogen, inclusive of all working expenses, amortisation of the concentrating section at an equated value of 8 per cent., but exclusive of interest on capital.

The final production cost of concentrated nitric acid by the arc process will thus be, per metric ton of acid calculated as 100 per cent.:

£2·5 + £2·0 + cost of 1·87 kilowatt-years of energy = £4·5 + 1·87 E.

With various costs (E) of energy per kilowatt-year, the costs of the concentrated acid will therefore be:

	£	£	£	
Cost of energy per kilowatt-year E ..	1·2	3·75	5	8
Cost per metric ton acid	6·744	11·512	13·85	19·46

These figures may be compared with the *pre-war* cost of acid made by the retort process from Chile nitre—viz., £22·3 per metric ton of acid (as 100 per cent. HNO_3) with nitre at £10·5 per metric ton. Under war conditions the cost of nitric acid made by this process rose to £35 per ton.

Although the figures quoted seem to indicate that even with coal as the source of energy the arc process would not be at a disadvantage *with natural nitre*, it must not be forgotten that in competition with *other synthetic processes* under the same conditions it might be at a decided disadvantage. In the United States, again, the development of fixation processes other than the arc has been retarded until the hydro-electric schemes are completed; it must therefore be evident that the use of coal as a source of energy is not regarded as satisfactory under the conditions there obtaining. As regards labour, the arc process is not disadvantageous, since the labour employed is comparatively small in comparison with the output.

A comparison of the costs of production of nitric acid by the arc process and from Chile nitre by the Valentiner process (p. 54), based on the figures of the Nitrogen Products Committee, is made by Hagemann (*Chem. Trade Journal*, January 13, 1922). The capital cost of the factory for 20,000 kilowatts is taken as £150 per ton of fixed nitrogen. The cost of production of 1 ton of 65 per cent. nitric acid, with power at £7 10s. per kilowatt-year, is given as £16. This corresponds with acid made by the Valentiner process with sodium nitrate at £9 per ton. Sodium nitrate, at £17 10s. corresponds with power at £12 12s. per kilowatt-year.

SECTION IV

THE OXIDATION OF AMMONIA

The Oxidation of Ammonia.

WITH the fixation of atmospheric nitrogen as ammonia by the Haber or cyanamide process, the problem of supplying the needs of industry for fixed nitrogen has been only partly solved. It has already been stated (p. 32) that the fertilising value of nitrate nitrogen is somewhat superior to that of other forms of available nitrogen, but in this respect the necessity for nitrate nitrogen is not imperative. Although ammonia nitrogen is somewhat less effective, the difference is only slight, and would be compensated by greater cheapness of ammonia nitrogen as compared with nitric nitrogen, when both were equally suitable from an agricultural standpoint.

In other industries, however, the case is different. The manufacture of dyes, drugs, and explosives imperatively requires fixed nitrogen in the form of nitric acid, usually as concentrated as possible. In peace conditions the demands of agriculture are by far the largest, but in time of war enormous quantities of nitric acid are consumed in the manufacture of guncotton, cordite, picric acid, trinitrotoluene (T.N.T.), nitroglycerin, and ammonium nitrate, among other products. A nation which is to be self-supporting in time of war must therefore, even if ammonia from fixation processes is available, possess the means of converting this ammonia into nitric acid. The conversion of ammonia into nitric acid is a process involving oxidation, as is seen by comparing the formula of ammonia, NH_3, with that of nitric acid, HNO_3, and the process by which this conversion is carried out is known as the "oxidation of ammonia."

All the processes for the oxidation of ammonia in use depend on the same principle. A mixture of gaseous ammonia with air or oxygen gas is passed over a catalytic agent, such as platinum, maintained at a suitable temperature, usually a red heat, when the ammonia is burnt primarily to steam and the colourless gas nitric oxide:

$$4NH_3+5O_2=4NO+6H_2O.$$

When the gas coming from the "converter" or apparatus in which the above catalytic reaction is brought about is cooled in presence of an excess of air or oxygen, the nitric oxide undergoes further oxidation into red fumes of nitrogen dioxide:

$$2NO+O_2=2NO_2 \text{ or } N_2O_4.$$

The gases are then brought in contact with water, also in presence of excess of air or oxygen, when a complicated series of chemical changes takes place, leading ultimately to the formation of dilute nitric acid, not exceeding 50 to 60 per cent. strength:

$$2NO_2+O+H_2O=2HNO_3.$$

This acid may be used directly for the preparation of nitrates, such as ammonium nitrate, or may be concentrated. The concentration is usually effected by distilling with concentrated sulphuric acid.

This is, briefly, the process used in the oxidation of ammonia. It consists of four distinct stages: (i.) The oxidation of ammonia catalytically to nitric oxide; (ii.) the spontaneous oxidation of the nitric oxide to nitrogen dioxide; (iii.) the absorption of nitrogen dioxide, in presence of oxygen (*e.g.*, air), in water to produce dilute nitric acid; (iv.) the concentration of dilute nitric acid.

The fact that ammonia can be converted into nitric oxide by passing the gas over heated manganese dioxide was discovered in 1788 by the Rev. I. Milner, of Cambridge. This was followed by the better-known experiments of Kuhlmann, professor at Lille, in 1839. The latter passed a mixture of ammonia and air over heated platinum. Nitric oxide is first formed: $4NH_3+5O_2=4NO+6H_2O$. If the moist gases are cooled, in presence of excess of air, nitric acid is ultimately formed: $2NO+3O+H_2O=2HNO_3$. The conditions under which this reaction takes place with a practical yield were elucidated by Professor Ostwald and Dr. Brauer in 1900, and patents were taken out in 1902. It was found that the gases must be passed rapidly over the catalyst, as otherwise a considerable amount of the nitrogen of the ammonia is liberated in the elementary condition: $2NH_3+3O_2=2N_2+6H_2O$. Under suitable conditions over 90 per cent. of the nitrogen is recovered as oxides. It will be noticed that all these discoveries were made by "academic" chemists.

A plant based on the discovery of Ostwald and Brauer was in constant operation for some time at the works of the Lothringen Colliery Company at Gerthe, near Bochum, which produced upwards of 1,800 tons of nitric acid or 1,200 tons of ammonium nitrate annually.

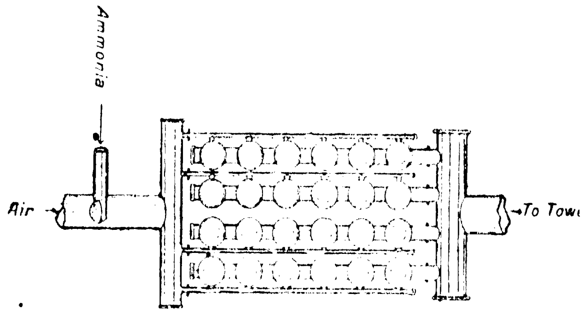

Fig. 19.—Ostwald Ammonia Oxidation Converters. Plan showing Concentric Tubular Catalysers, Arrangement for mixing Air and Ammonia, and Connections.

Carefully purified ammonia gas was mixed with air and passed through enamelled iron tubes to the catalyser. This (Figs. 19 and 20) consists of an inner vertical nickel tube surrounded by an outer tube of enamelled iron. At the top of the 2 inch nickel tube is placed a roll of crinkled platinum foil, about 2 centimetres wide, weighing about 50 grammes, which serves as the catalyst. This is first heated by a hydrogen flame introduced through a lid at the top, and the mixture of air and ammonia, containing not more than 9 per cent. by volume of the latter, is passed into the outer jacket. This passes through the platinum catalyst, and down the nickel tube, the heat given out in the reaction being communicated to the inflowing gas, so that no external heating is required when the reaction is once started. The gases are then passed through stoneware cooling tubes, and then into large granite or brickwork towers, packed with earthenware filling, over which weak nitric acid is circulated. The acid running from the first tower contains about 40 to 55 per cent. HNO_3. It may be converted into ammonium nitrate, or concentrated.

The Ostwald patents (which were not granted in Germany owing to the prior work of Kuhlmann) were taken over by the Nitrogen Products Company, and works were erected at Dagenham Dock, on the Thames, and at Angoulême in France. The ammonia for these works is produced from cyanamide.

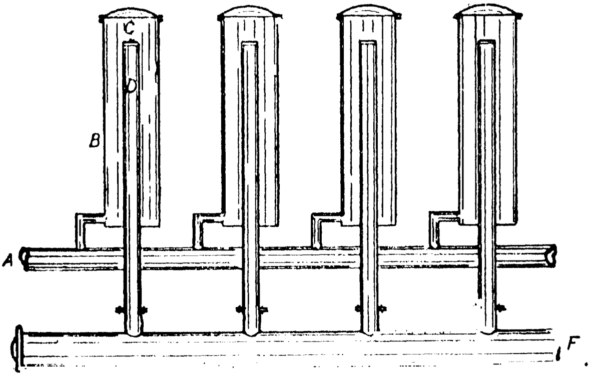

FIG. 20.—OSTWALD TYPE AMMONIA OXIDATION CONVERTERS.

A, Inlet main for mixture of ammonia gas and air; *B*, outer enamelled iron jacket with hinged lid *C*; *D*, inner nickel tube, at the top of which the platinum catalyst is supported; *F*, aluminium main collecting oxides of nitrogen from the converters.

At the newer French ammonia oxidation works at Bassens the air is taken in by suction through filters composed of thin rectangular boxes with flannel sides by means of two blowers delivering 7,000 cubic metres per hour each. The air and ammonia gas are mixed in a vertical cylindrical iron mixer, 6 feet in diameter and 20 feet high, containing baffle plates, with two inlets placed tangentially at the bottom and an outlet at the top. The mixture contained 1 volume NH_3 to 11 volumes air.

The converters were arranged on a floor above in eight groups of six to form a battery:

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Each half of the battery has its own inlet and outlet mains. Twelve batteries of forty-eight units are arranged in one house, and twelve in one house and twelve in a second house, each being served by a separate gasholder for ammonia.

The gas from each main coming from twenty-four converters by aluminium mains enters at about 200° C. two large U-tubes of silicon iron, 18 inches in diameter and 20 feet high, with two vertical outlets below. These tubes are cooled by a shower of water and the gas leaves at 80° C. It then passes to a series of six pottery U-tubes, about 18 inches in diameter, placed in a water-bath with partitions to cause circulation of cooling water. Inside the U-tubes are vitreosil tubes closed at the bottom, acting as Hough's condensers, about 6 inches in diameter and 16 feet long. Beyond these six U-tubes are seventeen U-tubes with internal cooling, but exposed to the air. The water from the internal coolers of these passes to the trough of the first six tubes. The outlets from four batteries of tubes are joined in a rectangular trough of volvic lava, from which a single 24-inch pottery main leads the gas, cooled to 40° C., to a set of six absorption towers, one set of towers to four semi-batteries of twenty-four converters each Preceding each set of six towers are four empty oxidation towers in parallel, consisting of stoneware pipes, 18 inches in diameter and 20 feet high. Owing to the heat of oxidation of the NO, the gas leaving these towers was still at 40° C.

The absorption towers are of acid-resisting brick laid in silicate and sand mortar with iron strengthening bands. They are 4 metres internal diameter and 12·5 metres high. Joints are made with a soft mixture of asbestos, sulphur, and tallow. The gas passes into the bottom of each tower, down through an internal pottery pipe of 12 inches diameter to the bottom of the next tower. The packing is of quartz lumps, all the same size, 6 inches in diameter. The gas pressure is 6 to 7 centimetres of water at the entry to the towers. Acid is circulated in each tower by two Kestner automatic montejus per tower, delivering to the tops of the towers through aluminium pipes 2 inches in diameter. The circulation of acid per tower is 5,000 litres per hour. Towers 1 to 3 are cooled by passing the acid leaving them in a shower over a battery of glass tubes enclosed in a box of volvic lava with cold water running through the tubes. The reaction is intense in the third tower. The final acid is 33° Bé. The exit gas from the towers contains 4 grammes NO per cubic metre.

The converters themselves are simple in construction, provided the necessary materials are at hand, and appear to work well. No extra heating of the catalyst is required, the reaction supplying the necessary heat when once started by a hydrogen flame.

On the other hand, the necessity of making the inner tubes of weldless pure nickel militates against this type of converter in England at the present time. A large quantity of platinum in the form of foil is also required, and consequently the output of nitric acid per unit weight of platinum is small. It is, moreover, impossible to use a richer mixture of ammonia with air than 9 per cent. by volume, as otherwise the catalyst becomes overheated. The flow rate per unit area of the converter tube is also very low. The conversion efficiency has been variously stated to be anything from 65 to 95 per cent., but at the converter itself it may be assumed that 90 per cent. is possible under proper conditions of working.

The Frank and Caro Converter was first put on the market in small units by the German "Bamag" firm for use in supplying oxides of nitrogen to lead-chamber vitriol plants. From the point of view of efficiency and general conditions of working, this type compares favourably with most other types of converters. The catalyst consists of a single platinum gauze electrically heated, which necessitates a slower flow rate and consequently lower output than later converters using several gauzes as a catalyst. These were introduced by Kaiser.

Kaiser Converter.—In this several platinum gauzes are placed close together, and the air is preheated to 300° C. in a coke furnace, being mixed with the ammonia 50 centimetres in front of the catalyst. Kaiser claimed larger yields with this converter than any other type, owing to auto-oxidation of atmospheric nitrogen itself. This, however, has not been substantiated, and the only advantage of this type over previous ones is the use of several gauzes to comprise the catalyst, which permits of a larger output.

The Solvay Process Company, Syracuse, N.Y., evolved a converter on the Frank and Caro principle. The converter consisted of a simple rectangular aluminium box with a single platinum gauze catalyst, heated electrically. It suffered from the same disadvantage as the original Frank and Caro type.

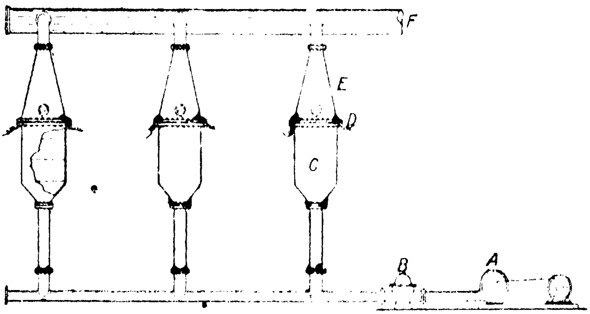

FIG. 21.—FRANK AND CARO TYPE OF AMMONIA OXIDATION CONVERTERS.
A, Fan; *B*, meter; *C*, body of converter; *D*, electrically heated platinum gauze catalyst; *E*, aluminium hood with mica window; *F*, outlet main for oxides of nitrogen.

The American Cyanamid Company designed a converter of much the same type as the Solvay Company.

Experiments made by the authors in the winter of 1916 resulted in a converter which appeared to be an improvement on previous types. This converter was designed on the Frank and Caro principle with the addition of a multiple gauze catalyst, as in Kaiser's apparatus. Two gauzes were found to be sufficient for 95 per cent. oxidation of ammonia with a high output of nitric acid per unit weight of platinum. The capital cost of the complete converter is only 10½d. per pound of HNO_3 per twenty-four hours. The chief advantages of this converter lie in the fact that both the flow rates and the composition of the air-ammonia mixture can be varied within wide limits without affecting the efficiency of oxidation. A small amount of electrical heating is required to be applied continuously to keep the yield up to 95 per cent. In later experiments the mixture of air and ammonia was preheated to about 500°, and no electric current was then required.

From actual experience it has been found that very little attention is required once the reaction has started, and provided due precautions are taken to prevent the access of dust, etc., to the converter, the catalyst remains efficient for many months.

It is necessary to obtain skilled and experienced workmanship in the assembling of the unit, but after that practically no further attention is required.

The Gas, Light, and Coke Company, of Beckton, claim to have conducted experiments with a platinum converter in 1908. It appears, however, that their efforts were not successful until about August, 1917, when a converter was evolved with four gauzes. Particulars of the catalyst used by the authors and an account of their experiments were given to the Gas, Light, and Coke Company early in 1917. The converter itself consists of a double pyramid of aluminium, later enamelled iron, and the catalysis is started by means of a pilot light. It was stated that the conditions of flow rate and air-ammonia mixture have to be kept within very narrow limits, which is not in accordance with the results of other users of similar apparatus.

Messrs. Brunner, Mond, and Company, who were made acquainted with the early work of the authors in March, 1917, and were provided at the time with an actual converter, found that this type of converter was very advantageous for use with vitriol chamber plants. They further modified the design of the converter, making it of silvered brass or nickel, in which the gas flow was downwards instead of upwards, and used four gauzes instead of two. Moreover, preheating of the gases was used, the catalyst itself not being supplied with any heat except that from the reaction itself. The efficiency was 75 to 85 per cent.

The United Alkali Company, of Widnes, also adopted the authors' pattern converter for experimental purposes, and as a result installed modified and improved types in their sulphuric acid plants. In the later patterns (see *J. S. C. I.*, 1922, **41**, 37T) the heat of reaction in the converter is used to preheat the mixture of ammonia and air. The converter is of iron, enamelled or coated with protective material, and the platinum gauze is vertical. This type of apparatus may be regarded as the most satisfactory form for use with air and ammonia.

At *Kharkoff, in Russia*, a plant was set up for the oxidation of ammonia just before the war, in which the converter consisted of an iron tube with a catalyst of platinum gauze (number of gauzes unknown) stretched across it. The mixture of air and ammonia was preheated to 150° to 300° C. The great disadvantage of this type of converter is the wear and tear on the platinum, due to iron oxide dust carried by the gas stream. It is stated that the gauzes had to be renewed every three weeks. The efficiency and output appear to have been good.

Another type of converter has been evolved in America, in which a cylinder of platinum gauze, open at the top for the gas inlet and closed at the bottom by a silica plate, is suspended in a chamber lined with glazed bricks. The heat evolved is said to be available for heating the entering gas. So far as is known, this type of apparatus is not in use on the large scale.

Ammonia Oxidation in Germany.

The output of nitric acid by ammonia oxidation from German works is given below:

NITRIC ACID (METRIC TONS HNO_3 PER DAY).

	1914.	1918.
Leverkusen	56	180
Höchst	150	375
Oppau*	?	100
Ludwigshafen	40?	40
Weiler ter Meer	12	24
	258	719

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* Can now supply 500 tons HNO_3 daily, and still supply NH_3 for oxidation plant at Höchst.

The Leverkusen Works of Farbenfabrik vormals F. Bayer.

Before the war there were two works belonging to the Bayer Company, at Leverkusen and Elberfeld. The Leverkusen works was the larger, employing 6,500 workpeople, together with a staff of 1,500 chemists, engineers, clerks, etc., and the number of workmen was increased by 1,500 during the war. This works produced dyes and intermediates, together with the necessary acids. The works at Elberfeld produced drugs, which were packed at Leverkusen; it employed 1,500 workmen, decreased to 1,000 during the war on account of overcrowding. The erection of the works at Dormagen, on a site acquired before the war, was completed early in 1917.

The Leverkusen works is situated on the east bank of the Rhine, about ten miles north of Cologne. The site, purchased about 1894, covers an area of some 400 acres, with a wharf on the Rhine and excellent railway facilities, both inside the works and in connection with the main lines. The water required in the works is obtained in abundance at a depth of about 100 feet, and the whole site has been filled up to 4 feet above ground level.

There are four sections of the works, and research laboratories, lecture-room, hospital, etc. During the war an entirely new plant for the manufacture of ammonium nitrate was erected at Leverkusen. The quantity of nitric acid made at this works amounted to 75,000 tons per annum, partly from sodium nitrate made by the oxidation of ammonia (60,000 tons) and partly from 50 per cent. nitric acid (15,000 tons) from the same source.

The ammonia oxidation plant at Leverkusen was erected early in the war to replace the supply of Chile nitre, the plans being supplied by the Badische Company at Ludwigshafen. The ammonia came partly from synthetic sulphate and partly from gas liquor. The ammonium sulphate was dissolved on one side of the works in twelve dissolvers of 1,000 gallons capacity, and milk of lime was prepared in a parallel row of vats on the other side. Between were two rows of ten ammonia stills in each, also of about 1,000 gallons capacity, fitted with agitators and steam coils and leading to a common main of

18 inches diameter. Gas liquor was distilled from milk of lime in vertical stills of six effects, the steam coils being in the bottom section.* Four columns were installed. The ammonia gas was passed through a similar vertical column scrubber, in which it was washed with caustic soda solution. There were two scrubbers, 5 feet by 12 feet; the stills were 15 feet high and 4 feet in diameter.

The ammonia gas was passed through a small balancing gas-holder of 500 cubic feet capacity into a large holder of 1,000 cubic metres capacity with an indicating dial. A mixture of air and ammonia containing 7 per cent. of ammonia was driven by separate centrifugal blowers to the converters, the air being filtered through cloth. Venturi meters controlled the mixture, which contains 7·5 per cent. by volume of ammonia. The air passed through a cylindrical tubular heat exchanger (B.P. 145,059/1920), 12 feet by 12 feet, in counter-current to the hot converter gas, leaving by an 18-inch pipe; a 6-inch by-pass being also provided. The ammonia was not preheated, but passed by a 4-inch pipe to a mixing chamber between the exchanger and converter. This mixing chamber in some cases consisted of an inclined cone 3 feet long and 4 feet in diameter, the hot air entering the base and the ammonia and cold by passed air tangentially. The mixture passed to the converter at 300° to 360°.

The converters are sheet-iron cylinders lagged externally and lined with bricks, 15 feet high and 12 feet external diameter. They formerly had an axial tube 3 feet in diameter serving to convey cold air to equalise the temperature of the catalyst, but in the newer types, which have a diameter 1⅓ that of the older, this axial tube is omitted. The catalyst layer is deep, so that the time of contact is much longer than with platinum. There are first about 10 inches of fine granules resting on coarser granules on a perforated refractory plate. The gas passes upwards through the catalyst. The diameter of the catalyst granules varies from 5 to 10 mm. The diameter of the catalyst bed in the older type was 9 feet, the drop of pressure across it being about 10 centimetres of water. The temperature of the catalyst is about 750° C. The average capacity of the older units was 4,600 kilogrammes ammonia per day; the new converters have a capacity of 15,000 kilogrammes per day. The capacity of the whole plant is 6,000 to 7,000 tons of sodium nitrate per month, with an efficiency of 80 to 85 per cent. over-all. The catalyst, provided by the Badische Company, consists of oxide of iron with promoters. The writers, with Dr. E. K. Rideal, tested a large number of catalysts of this type in 1916. The mixture of oxides of iron, bismuth, and cerium described in the patent specifications of the Badische Company was found to be an efficient catalyst (90 per cent.) in thick layers at higher temperatures, but the bismuth oxide slowly volatilised.

The absorption plant for oxides of nitrogen consists of three distinct units. These effect absorption in sodium carbonate, in water, and in sulphuric acid respectively.

In the alkaline-absorption section each converter is connected with six towers, the first a small rectangular stone tower 12 feet high and 3 feet side, acting mainly as a cooler; the second tower is cylindrical, 30 feet high, and 8 feet in diameter, of steel plates; the third tower is rectangular, of volvic stone, and 30 feet high; whilst the remaining three towers are like the second. There are twelve rows of these towers, the gases from which passed by a common main to a 60 foot tower, 20 feet in diameter, through which they were drawn by a fan. Saturated sodium carbonate solution was supplied to the tops of the first, second, sixth, and seventh towers, and drained to a granite tank, from which it was pumped to the top of the fourth tower, which was run slightly acid so as to cause conversion of all nitrite into nitrate. From this tower the sodium nitrate solution left by a 4-inch main.

In the water-absorption section, erected in 1918, the gas from the converters is brought by a 3-foot main to six brick towers, 40 feet by 12 feet, arranged in three rows of two and packed with broken quartz. From these the gas passes through a rectangular brick flue, 6 feet by 3 feet, to twelve brick towers, 60 feet high and 13 feet internal diameter, the walls being 2 feet thick. After being drawn through these towers by a fan, the gas is discharged to the free air through a 3-foot iron pipe. Water is fed to the last tower and circulated forward by centrifugal pumps. When the acid reaches the bottom of the fourth tower in the series of twelve it is cooled between successive towers and finally reaches a concentration of 40 to 50 per cent. nitric acid.

The latest plant is for absorption in sulphuric acid. There are six steel towers, 40 feet high and 8 feet in diameter, the acid being cooled in coils between each pair of towers through which it is circulated.¹ Nitric acid is recovered by distillation, although steam must be added. The results agreed with those found by the writers in laboratory experiments—viz., that sulphuric acid absorption is not efficient on account of the difficulty of recovering nitric acid from the liquid after absorption.

The ammonia oxidation plant at Oppau consists of more than one set. One set consists of twenty oxide catalyst converters in two rows. Each unit uses 8 tons of NH_3 per day, and the oven measures 18 feet by 15 feet. The catalyst layer is 1 foot deep on a perforated partition of refractory material. The temperature is 800°. The ammonia air mixture passes through two vertical heat exchangers 20 feet by 4 feet, and enters the top of the converter normally. The hot gas passes through a boiler 8 feet by 5 feet, then through an economiser 6 feet by 4 feet to the heat interchangers. Two catalyst furnaces are used in parallel with one boiler, one economiser, and one pair of heat exchangers. The gas was preheated in the basement to 200° for starting. The refractory lining of the converter is 1 foot thick; there is no central cooling flue. The exit pipes, 2 feet in diameter, are lagged with diatomite brick.

The absorption plant is composed of three rows, each of two brick towers 80 feet by 20 feet, two granite towers 80 feet by 15 feet, and two steel towers 80 feet by 15 feet, in the order given. Soda solution was passed to the steel towers, which were packed with quartz. Krupp's chrome steel acid pumps are used, the acid being distributed by jet sprays. The granite towers were dodecagonal, resting on jointed bases 3 feet thick. The slabs were joined with cement with **H**-girders, bars, and bolts.

Concentration of the acid is effected by sulphuric acid, giving 99 per cent. acid. The sulphuric acid is reconcentrated in Kessler's and vacuum apparatus.

Ammonia Oxidation at Höchst.

The ammonia oxidation plant of the Höchst Farbwerke (vormals Meister, Lucius und Brüning) is situated at Höchst, on the right bank of the Main, about ten miles from Mainz. It is about two miles from the works of the Griesheim-Elektron Company, with which, however, it has no connection. During the war an amalgamation with the Badische interests took place, synthetic ammonia from Oppau being supplied to Höchst for oxidation. There was before the war an oxidation plant at Höchst, comprising thirty-seven converters fitted with circular platinum gauzes about 7·2 inches in diameter, contained in vessels similar to those used for contact sulphuric acid. The efficiency of this plant, which produced about 54,000 tons of nitric acid per annum, was not above 80 per cent., and a new plant, completed in February, 1919, was erected in its place at a cost of about £1,000,000. This plant has a capacity of 24,000 tons of ammonia, or 140,000 tons of nitric acid, per annum.

In addition to synthetic ammonia, arriving as 25 to 27 per cent. liquor from Oppau, gas liquor ammonia (20 per cent. NH_3), and cyanamide ammonia liquor (22 to 27 per cent.) from Knapsack, were received, the liquor being stored in four overhead spherical steel tanks, each of 264,200 gallons capacity. The liquor was rectified in four stills, one spare, of the Savalle type with fifteen effects, each with a capacity of 20 tons of ammonia daily. The gas not used for oxidation was absorbed in a plate tower 30 to 40 feet high. Ammonia from gas liquor was scrubbed with caustic soda solution of 48° to 53° Tw., and then passed through charcoal purifiers in the usual way to remove sulphur compounds. The ammonia gas from the stills was freed from moisture by refrigeration with ice-cold water; the presence of moisture caused scaling of the iron pipes, and was also believed to be prejudicial to the conversion, although there is no evidence of this.

The ammonia gas and air were metered through Venturi meters and driven by ten 55-kilowatt centrifugal blowers to the filters and converters. The mixture contained 12·5 per cent. by volume of ammonia, regulated within narrow limits.

The ammonia supply pipe was 6 inches in diameter and the air pipe 18 inches in diameter. The air was filtered through cloths in a wooden box, and the mixed gas was carefully filtered

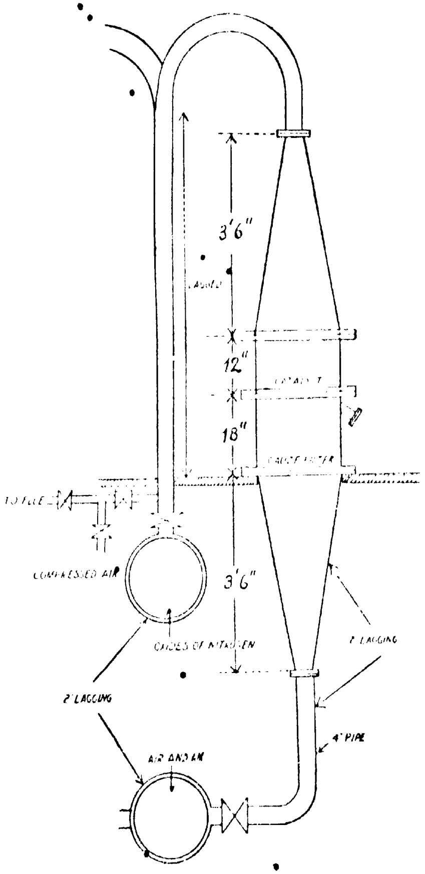


FIG. 22.—DIAGRAM OF AMMONIA OXIDATION CONVERTER WITH PLATINUM CATALYST AS USED AT HÖCHST.

from dust and ammonium salt fumes through eight layers of linen cloth in chambers 9 feet by 5 feet.

The gas passed under 6-inches water pressure through two central mains in the converter house, from which it was diverted to the 224 converters, each provided with a circular platinum gauze catalyst of 20 inches diameter, or 2·12 square feet cross-section. The maximum output of each converter was 1·5 tons of nitric acid per twenty-four hours, the efficiency of oxidation being 89 per cent. The efficiency from ammonia to dilute acid (including the efficiency of the absorption plant) was 87 per cent.; that from ammonia to strong acid (including the concentrating plant) was 84 per cent. The body of the converter (Fig. 22) consists of cast iron, in four sections with flanges. The two middle sections were 18 inches and 12 inches high, and supported the catalyst between them; the conical top and bottom pieces were each 3 feet 6 inches high. The top cone was lined with sheet nickel to protect it from the hot gas. The catalyst, clamped between asbestos rings, was started by heating to redness by a hydrogen or coal-gas flame inserted below it through a lighting hole shown in the figure.

The exact construction of the catalyst has been differently stated. It has been asserted that it consists of two, or three, or four platinum gauzes, 20 inches in diameter, of 0·06 mm. wire with 80 meshes to the linear inch. The gauzes are possibly spot-welded and are supported on a grid of ten stout platinum wires, 1 mm. in diameter, spaced at 10 centimetres distance. The total weight of platinum in the catalyst has been stated as 333 grammes, which does not agree very well with the details of construction, but is probably approximately correct.

The converters were arranged in two sets of seven or eight on each side of separate inlet and outlet mains, the latter 1 foot in diameter and connected with the converters by 4-inch pipes lagged with diatomite brick shaped to fit, cemented and wired. The upper bend pipe of the converter was not lagged, so as to allow for expansion. Before entering the converters the gas passed from a common main to a vertical, lagged, multitubular preheater, 15 feet by 5 feet external dimensions, in which it was heated by steam. The purpose of this was to prevent condensation of acid from the hot gases coming from the converter when these were passed through the heat exchanger which followed. In this, which was identical in dimensions with the preheater, the warmed gas passed in counter-current to the gas from the converters, and left at 200° C. Two heaters so arranged served fourteen converters. The temperature of the catalyst was about 800° C.; the gas left the converter at 650° to 700° C. In starting the converters extra air could be added and the only partly converted exit gas by-passed to a chimney until the gauze was activated. Gate valves were used, with a slight air pressure on the side of the valve not in contact with the gases, to prevent leakage. In fifty-six of the latest type of converters the gas was passed by a lagged 3-foot main through two tubular boilers, leaving these at 270° C. to the heat exchanger. In this way 4 tons of water were evaporated per hour and the steam was used for warming the gas, as described above. From one to three men only are necessary to attend to all the converters.

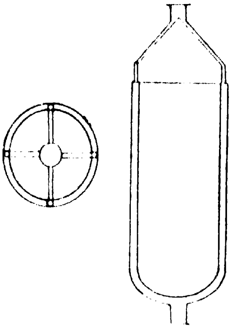


FIG. 23.—INTENSIVE COOLER FOR GASES FROM AMMONIA OXIDATION CONVERTERS AS USED AT HÖCHST.

The gases containing nitric oxide and steam coming from the converters were passed through eight cast-iron mains 18 inches in diameter, supported on three ferro-concrete bridges, to four rows of eight absorption towers. Each row of towers was provided with twelve intensive coolers of special design—*i.e.*, forty-eight coolers in all. These coolers (Fig. 23) were of aluminium, with an annular space between the outer wall and an inner vessel, the gas entering above through a

4-inch inlet, dividing into four 2-inch pipes leading to an annular space between the walls. The gas and condensate left through a 4-inch outlet below. The coolers are 5 feet high and 2 feet 6 inches in diameter. In them, on account of the rapidity with which the gas passed through, practically no acid was condensed, but only water. The condensate was put down the fifth absorption tower. The gas left the set of four coolers at 30° C. through four pottery mains 1 foot in diameter, joining to a single brick chamber at the base of each set of eight towers attached to fifty-six converters. Secondary air was admitted at this point (not before the coolers).

The towers are 41 feet high and 21 feet in diameter internally. The walls comprise three layers of brickwork, the outer layer of bricks 6 inches by 4 inches, set in a mixture of sodium silicate and kieselguhr. The top of the tower is slightly domed, and there is a central partition in each tower, the gas passing up one side and down the other, and then going to the next tower through a brick channel at the base. The towers are packed with stoneware rings. The total internal volume of all the towers is 35,320 cubic feet, which amounts to only 81 cubic feet per pound NO_2 absorbed per minute, as compared with 350 cubic feet calculated by the formula proposed by the writers (*J. C. S. I.*, 1919, **38,** 75T), or 1,500 cubic feet as used at the French works at Bassens when we saw it in 1918. The reason why this small tower capacity is effective is clear when it is remembered that at Höchst no less than 25 per cent. of the oxides was absorbed as nitrate by saturated sodium carbonate solution fed to the last two towers. The liquor in the first of these towers is allowed to become acid, so that the nitrite is converted into nitrate, whilst that in the second is kept alkaline, to absorb the oxides of nitrogen driven out of the first when conversion into nitrate occurs (see B.P. 129,699/1919; Partington and Rideal). The solution of nitrate was evaporated by the waste heat of the converters. The remaining towers were fed with water for the production of nitric acid. The efficiency of absorption plant was 97 per cent. Each tower is stated to have cost 40,000 marks. Acid of

50 per cent. strength was obtained from the first tower of the series, the liquid being circulated in the towers by 8-inch chrome steel centrifugal pumps, each fed by a 3 to 4 inch pottery main and delivering through a silicon-iron pipe of the same diameter to the top of the tower, two delivery pipes being used to each tower. The metal pipes were coned and fitted in the same way as the pottery pipes. Acid distribution was effected at the top of the tower by a revolving ribbed disc, turned by a gear shaft at 80 r.p.m.

The acid from the towers was passed to the coolers, consisting of S-pipes of silicon iron cooled externally with water. There were also intercoolers between each pair of towers except the last, and the temperature was kept as low as possible, 25° C. in winter and 40° C. in summer. The fact that the dilute acid towers would probably work slightly better if warm (see Partington and Parker, *loc. cit.*) does not seem to have been appreciated. In summer iced water was used in the coolers. Large stoneware receivers were placed above the coolers to serve as acid reservoirs. The circulation in each tower was 110 gallons per minute; the loss of acid in the whole system did not exceed 2 per cent.

Twelve stock tanks of brickwork, each holding 1,412 cubic feet, received the tower acid, from the receivers at the base of the towers, through tapered pottery pipes. No fan was used with the towers.

The tower acid was concentrated by mixing 1 part of 50 per cent. tower acid with 7 parts of sulphuric acid, in five mixing vessels with mechanical stirrers, and then denitrating. About 42,000 tons of sulphuric acid was used per month, but practically all was recovered. (In France 2·5 to 3 parts of sulphuric acid only were used, but the nitric acid obtained was less concentrated (85 per cent. strength) than that obtained at Höchst.) The nitric acid was recovered partly in two rows of nine silicon iron towers, 4 feet in diameter and 25 feet high, and partly in stone towers, with cast-iron pipe jackets, 35 feet high and 3 feet 6 inches external diameter, the walls being 9 inches thick. Steam at 150° C. was introduced at the base by a 1-inch lead pipe just above the exit for the denitrated acid. The nitric acid vapour from the top of the denitrator passed to a cooler of **S**-shaped silicon-iron pipes. The acid to be denitrated entered halfway down the cooler, and acid from stock was sent down the upper part to assist condensation. Oxides of nitrogen were removed from the nitric acid by a current of air and recovered in twenty absorption towers. The completely denitrated sulphuric acid was cooled in a water-cooled cast-iron cooler and collected in a large lead-lined tank of artificial stone. It contained about 70 per cent. sulphuric acid, and was reconcentrated in a Kessler apparatus or in a modified Pauling apparatus. The latter was said to be very efficient. (In French practice a denitrating column 20 feet high and 18 inches internal diameter produced 6 to 8 tons of nitric acid per day; with an over-all yield of 85 to 87 per cent. on the ammonia burnt in the Ostwald type catalysts. The consumption of fuel in reconcentrating the sulphuric acid was 15 to 20 per cent. of the weight of nitric acid produced.)

It is of interest to compare the mode of operation at Höchst, representing the latest German practice, with the indications obtained by experimental work in England, unfortunately never translated into technical practice. The resemblance is striking. In the following comparison the experiments carried out by the writers and their colleagues for the Munitions Inventions Department are referred to, many of which have not been published. The separation of water from the converter gas by rapid cooling was the subject of B.P. 131,942/1918 (Rideal and Partington). The object of this procedure, which is combined with the addition of secondary air *after* the coolers, is to keep the gas as concentrated as possible in the oxidation and absorption towers. It is clear from the equation, $4NH_3+5O_2=4NO+6H_2O$, that the uncooled converter gas contains nitric oxide and steam in the ratio 2 to 3 by volume, so that if the steam is removed a considerable concentration in oxides of nitrogen results.

The dimension of the platinum wire and the mesh of the gauze are also those found most suitable by the writers, and if the use of two gauzes at Höchst is the correct description this is also in agreement with the type of catalyst recommended in the official publication, "Ammonia Oxidation applied to

Vitriol Chamber Plants," M.I.D., Stationery Office, 1919. The use of alkali to finish the absorption was carried out exactly in the manner specified in B.P. 129,699/1919 (Rideal and Partington); it has been shown that this effected a considerable economy of tower space. The use of sulphuric acid as an absorbent, which was tried at Leverkusen and found unsatisfactory, was also the subject of a long series of experiments (unpublished) by the writers, who decided that it was not an efficient method of absorption.

It may fairly be said that laboratory workers in England and Germany seem to have been led to the same conclusions; but whereas the German technologists translated the results into plant, the English work finished in the research laboratory.

Ammonia Oxidation in America.

In the ammonia oxidation plant at Muscle Shoals (see p. 214) there are six converter houses and a meter room to each, the air being passsd by blowers through a 5½-foot duct and mixed with ammonia gas by meters in the ratio of 1 volume ammonia to 9 or 10 volumes air. The mixing is performed in twelve mild-steel mixing tanks, 8 feet in diameter and 30 feet high, packed with 6-inch spiral rings, from which the gas passes to the converters.

There are four rows of 29 converters in each converter house, or 696 in all, spaced 5 feet apart. The gas enters at the top through an iron pipe. The body of the converter is an aluminium box, rectangular in section, 14 inches by 28 inches, and 5 feet high. At the base is a single horizontal sheet of platinum wire gauze, of 0·003 inch wire and 80 meshes to the linear inch, weighing 4·6 ounces troy. Each gauze is heated by an 8-kilowatt transformer at 21 volts and 375 ampères to about 750° C. The converted gas passes down through an iron cone attached to the converter body and along an iron pipe to a concrete flue lined with acid-resisting tiles laid in acid-proof cement, leading to the coolers. Each converter produced 900 pounds of nitric acid per twenty-four hours.

The high-temperature coolers consist of twenty-four horizontal steam boilers at 25 pounds pressure. In passing through the tubes the temperature of the gas is reduced from

600° to 200° C. The gas then passes to low-temperature coolers, twelve of which are used, connected with the boilers by 30-inch aluminium pipes. Each low-temperature cooler is a rectangular brickwork chamber divided into five compartments by four walls which do not quite reach across, so that the gas is compelled to take a zigzag course. Suspended from the roof of each compartment are 140 tubes, 5 inches in diameter and 7 feet long, in two compartments of stoneware and in three of silicon iron. Each tube has an outlet lip at the top and an internal tube through which water flows. The gas is cooled on the outer surfaces of these tubes to 30° C., and some nitric acid is condensed, which drains off to No. 3 well of the absorption system.

From the coolers the gas passes to twelve oxidation towers, 15 feet square, of chemical brickwork, each divided internally by two walls into four compartments. The gas passes up one compartment, over the top of the dividing wall, down the next compartment, up the next compartment, and down the last. The practically fully oxidised gas now passes to the absorption towers. All the towers are housed. There are twenty-four absorption towers, 35 feet square and 60 feet high, of brick, divided into four compartments as before. The first tower of each unit of two is half packed with 6-inch spiral rings and half with 3-inch spiral rings. The second tower is completely packed with 3-inch rings. Water is circulated in counter-current to the gas and 50 per cent. acid is recovered from the towers. The acid is pumped by air lifts, each single-stage, throwing 50 gallons of acid per minute. One lift is provided for each compartment, or ninety-six in all, with twenty-four spares (see J. Oliphant, *Met. and Chem. Eng.*, 1920, 22, 408). To accommodate these lifts there are 120 iron wells, 12 inches in diameter and 100 feet deep. The lifts consist of 3-inch aluminium pipe (which was not found satisfactory in England for nitric acid) with silicon-iron flanges. The towers also stand in aluminium saucers. Air at 100 pounds pressure is supplied by a 1-inch pipe, and the acid in each well section is cooled by water flowing in the well. Leakage of acid is indicated by a signal lamp lighting up owing to increased conductivity. Between the two towers of each unit is an aluminium fan, and after the second tower a similar fan exhausts the residual gas to the free air. The compressed air from the lifts is also discharged into the free air, which must cause considerable loss of oxides of nitrogen and acid spray. The tower acid passes to twelve aluminium weighing tanks on scales, and is discharged to twelve storage tanks of acid brick and concrete, from which it is run off by a 3-inch aluminium siphon. When operating at full capacity the plant produces 280 tons of nitric acid per day.

Oxidation of Ammonia in Solution.

Numerous experiments have been made with a view to the practical utilisation of the bacterial oxidation of ammonia to nitrates, notably by Muntz and Lainé, of the Pasteur Institute, and by Lunden and Thorssell, of Stockholm (see p. 81).

The objections to such processes are their slowness, the space required for handling the enormous bulks of dilute solutions obtained, and the large amount of fuel required for the evaporation of the latter. Ammonia is much more easily oxidised to nitric acid by catalytic methods.

During the progress of the authors' work on ammonia oxidation for the Ministry of Munitions (1916-1918), the technical experts of the Explosives Supplies Department became greatly interested in a secret process for the oxidation of ammonia in solution which, according to vague reports by benevolent neutrals and American experts (*cf.* "A Statement of the Action Taken and Contemplate Looking to the Fixation of Nitrogen," Washington, 1917), was "worthy of very serious consideration," and was capable of giving a yield of 100 per cent. as "dry ammonium nitrate." The process worked out in this country was compared most unfavourably with the unknown process by the "experts," and efforts were made to acquire information from the Swedish inventors on reasonable terms. This was not found possible, and when, later, the process was disclosed, the public had reason for gratification that a large sum of money had not been offered in exchange for the wonderful "secret."

Ammonia Oxidation in Sulphuric Acid Works.

Towards the end of 1916 the Nitrogen Products Committee came to the conclusion that the ammonia oxidation process was well adapted, as an emergency measure, to securing quickly a considerable output of nitric acid or nitrates. Although already working more or less successfully upon the Continent, the process had not at that time been operated in this country. Apart from a few obscure patent specifications, there was no information available on which to base the investigations which were then begun.

A systematic investigation of the process was therefore undertaken by the writers, associated, at various times, with the following chemists: Dr. E. K. Rideal, M.B.E., Mr. G. J. Jones, Dr. G. N. White, and Mr. T. K. Brownson.

As the outcome of this research work, much useful information was collected, and in March, 1917, a conference took place at the Munitions Inventions Department, and was attended by representatives of manufacturers likely to be interested in ammonia oxidation. As the result, a small converter from the laboratory was installed by Messrs. Brunner, Mond and Company, in connection with the application of ammonia oxidation to the manufacture of sulphuric acid by the chamber process, which forms the subject of this section. Several other manufacturers also agreed to take up the study of the process with a view to its commercial development, and some of these have already erected plant and conducted experiments on a fairly considerable scale; in particular, types of apparatus for producing ammonia gas, which could not adequately be studied in the laboratory, have been designed and worked by the firms using the process. A small one, based on the design of that used by the United Alkali Company, was installed in the laboratory of the Munitions Inventions Department, and gave excellent results.

The experimental work in the laboratory was conducted throughout with converters of the size actually used on a technical scale, and the results were therefore based on practical experience. Although many problems yet remain to be solved, the successful operation of ammonia oxidation converters over a fairly long period, under actual works conditions, has shown that the process is well adapted for the purpose described.

A publication, which comprises an account of only a small part of the research work carried out in the laboratory of the Munitions Inventions Department on the oxidation of ammonia and the production of nitrates, was first issued in December, 1917, for circulation to Government Departments, controlled firms, and Allied Governments. As the outcome of further research, substantial revision was introduced into the new edition, which is now generally available. This official publication is entitled "The Oxidation of Ammonia applied to Vitriol Chamber Plants," Munitions Inventions Department, H.M. Stationery Office, 1919, price 1s. 3d.

The research work carried out by the authors and their colleagues on the oxidation of ammonia for the Munitions Inventions Department is largely unpublished. It comprised the following investigations:

First General Report.

(i.) Preliminary experiments with numerous catalysts.
(ii.) Experiments with platinum gauze catalyst.
(iii.) Analytical methods.
(iv.) Absorption towers.
(v.) Use of lime as a solid absorbent (first series of investigations)
(vi.) Miscellaneous technical details.

Second General Report.

(i.) Influence of composition of air-ammonia mixture and flow rates on efficiency of oxidation.
(ii.) Analytical control of ammonia oxidation.
(iii.) Use of liquid solvents for the absorption of oxides of nitrogen.
(iv.) Absorption of oxides of nitrogen in water and dilute nitric acid.
(v.) Use of solid absorbents for the oxides of nitrogen (second and third series of investigations).

(vi.) Concentration of aqueous nitric acid by nitrogen peroxide.
(vii.) Direct preparation of nitric acid by refrigeration of converter gas.
(viii.) Absorption of oxides of nitrogen by alkalies and alkaline earths, with production of nitrates.
(ix.) Absorption and drying of converter gas in sulphuric acid.

Third General Report.

(i.) Stability of ammonium nitrite.
(ii.) Direct preparation of ammonium nitrate from converter gas and ammonia:
  (*a*) Aqueous ammonia.
  (*b*) Gaseous ammonia.
(iii.) Production of ammonia from ammonium salts.
(iv.) Tower packing and design.
(v.) Flow sheets and technical applications.
(vi.) Conference of acid manufacturers, and application of ammonia oxidation to sulphuric acid manufacture.
(vii.) Visits to factories.
(viii.) Oxidation of ammonia gas and solution with oxygen and with air enriched with oxygen.

The information so obtained was, it is understood, communicated by the Government to Messrs. Brunner, Mond, and Company (see p. 178). An official publication will shortly be issued by H.M. Stationery Office giving an account of some of this work.

The oxides of nitrogen required to make good the losses in the catalytic process are supplied to the vitriol chamber in different ways: (1) As nitric acid obtained in the gaseous state by the decomposition of sodium nitrate and sulphuric acid in pots placed in the flue passing from the pyrites burners to the Glover tower (the so-called "potting process"; (2) the introduction of ready-made liquid nitric acid to the Glover tower; (3) the introduction of gaseous oxides of nitrogen, NO, N_2O_3, and NO_2, produced in special apparatus by the oxidation of ammonia, to the Glover or Gay-Lussac tower or chambers. The last method is comparatively new, but has been employed with great success in several works.

The advantages claimed for the old potting process, which is still used in a large number of works, are as follows: The chambers are not exposed to possible damage from liquid nitric acid; the handling of liquid nitric acid is avoided; the separate preparation of liquid nitric acid, which requires a separate plant, is rendered unnecessary; the irregular evolution of nitric acid from the pots can be more or less compensated by using several sets of pots and charging them in succession.

The advantages claimed for the use of liquid acid as compared with potting are greater economy (although exactly the opposite is sometimes claimed); the greater regularity and control assured by admitting liquid acid in a measured stream; avoiding the introduction of false air into the chambers and escape of chamber gases *via* the potting apparatus; the possibility of altering the proportion of nitric acid supplied within wide limits at short notice; and economy of sulphuric acid, since less is used in making nitric acid in stills than in the nitre pots.

The general conclusion is probably that the potting system and the use of nitric acid are pretty much on a level, but that both are superseded by the new process of introducing gaseous oxides of nitrogen from the oxidation of ammonia.

The use of oxides of nitrogen, directly introduced into the chambers or into the towers, appears to be the most rational method. In some cases waste gases from other manufacturing processes, such as the preparation of arsenic acid, or ferric sulphate, may be used, but such sources of supply, although they may be convenient ways of usefully disposing of nitrous gases, will not usually be regular enough for use in the vitriol plant. The most successful method is to generate the nitrous gases continuously by the oxidation of ammonia.

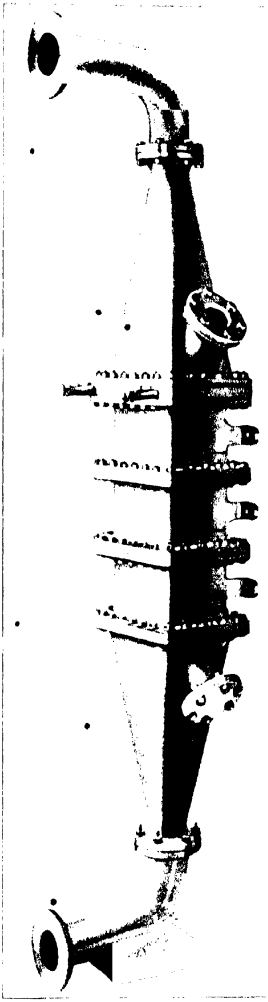
The first type of apparatus used in England for the purpose of supplying oxides of nitrogen to vitriol chambers was devised by the writers for the Munitions Inventions Department in October, 1916. The Munitions Inventions Department converter (Plate XVIII.) is constructed in a standardised size of approximately 4 inches by 6 inches internal section. It consists of a body of aluminium in three segments, having removable baffles between them, and an upper and a lower cone, also of aluminium, for exit and entrance of gases in the direction of flow respectively, the whole being fitted together with asbestos washers. Lugs are provided on the intermediate sections so that the complete converter may be mounted on suitable supports. At the top of the converter body there is a stout flange, on which is placed the platinum gauze catalyst unit subframe. The writers have also used with success a converter of good quality enamelled iron (supplied by the Cannon Iron Foundry, Bilston, Staffs). In this case, however, the whole must be warmed up before starting, as otherwise condensate formed inside the hood, containing traces of iron, runs down on the platinum, completely poisoning the latter. Oxide of iron is very poisonous to platinum in ammonia oxidation; the gauze ceases to glow and ammonia passes through unchanged.

When electrical heating is employed, the catalyst unit subframe (Plate XIX.) is composed of *two* platinum gauzes made of pure platinum wire, diameter 0·065 mm., evenly woven in square mesh, 80 meshes per linear inch. These gauzes are mounted in insulating supports of mica and asbestos. The lower gauze has silver leads with terminals for the heating current, and is surmounted by an exactly similar insulated plain gauze, the two gauzes being stretched and held separated by three or four silica rods, 0·5 mm. diameter, evenly spaced and recessed into the mica. The whole catalyst unit is screwed between two stout aluminium rings, having holes drilled so as to coincide with those in the flanges on the body and hood. The side of the catalyst bearing the stamped number should be uppermost.

When electrical heating is *not used*, the catalyst consists of *three* or *four* platinum gauzes of the same dimensions as before, stitched together with pure platinum wire to form a pad. This pad is mounted as before, between asbestos washers in the two aluminium rings.

Over the catalyst unit is placed the converter hood,

PLATE XVIII.



AMMONIA OXIDATION CONVERTER.

with a flange at the bottom for bolting through the catalyst subframe to the converter body. At the top is a circular flange, on which is bolted a similar flange on a bend tube. An asbestos washer is inserted between these two flanges, and *great care should be taken that no pieces of this washer fall upon the platinum catalyst.* The mica (or clear silica) inspection window is fitted to the side tube of the hood, with asbestos washers and the aluminium ring.

The mixture of air and ammonia, filtered and purified as described below, in the proportions of 1 volume of ammonia to 7·5 volumes of air, is passed to the base of the converter at a suitable rate—*i.e.*, approximately 6·2 pounds of ammonia, or about 1,200 cubic feet of mixture, per square inch of cross-section per twenty-four hours.

The apparatus is started by switching on the electric current of about 5 volts, 300 ampères, and heating up the gauzes to visible redness. The mixture of air and ammonia is then admitted *at a slow rate,* until the catalyser is seen to be *uniformly dull red-hot* (650° C.), then the rate is increased to the maximum, the current being reduced as necessary. Very little further attention is required for weeks of running. If the gauze gets too hot, the heating current, or the proportion of ammonia in the mixture, or both, should be reduced.

When electrical heating is not employed (and a 3-gauze catalyst therefore used), the apparatus is started up by heating the gauze to redness by means of a hydrogen or non-luminous gas flame inserted through the window aperture. The mixture of air and ammonia is turned on at the full rate, and when the reaction begins the heating flame is withdrawn and the window bolted into place.

New platinum gauzes are somewhat inactive, and should first be " activated " by passing at a fairly slow rate a mixture with an excess of oxygen—say 1 volume of NH_3 to 10 volumes of air—and putting on the full current till the gauzes are heated to *bright* redness (about 800° to 900° C.). After an hour or two the platinum becomes activated, and the white fumes of ammonium nitrite and nitrate leaving the converter (after cooling) change into clear red fumes of oxides of nitrogen. When this occurs the current is reduced and the ammonia brought up to the ratio of 1 volume of NH_3 to 7·5 volumes of air.

If no electrical heating is applied, the ordinary gas mixture is used from the start.

If spots are observed on the heated gauze in working, and these do not rapidly disappear, the catalyst should be taken to pieces, the gauzes boiled in pure hydrochloric acid, and the unit reassembled. If the gauzes heat up unevenly it is usually a sign that too thin wire has been used in their construction. It is necessary during the activation that the whole surface of the gauze should be uniformly heated. If cooler spaces—*e.g.*, near the edges—are left, these only very slowly become active on running.

As regards the working capacity of these converters, it may be taken that the efficiency of conversion of ammonia to oxides of nitrogen with electric heating of the catalyst or pre-heating of the gas is about 90 to 95 per cent., or 87 to 90 per cent. without electrical heating or pre-heating, and the capacity corresponds with a maximum output of 1·5 tons HNO_3 per square foot of converter cross-section per twenty-four hours.

The mixture of air and ammonia supplied to the converter may be produced in two different ways:

(1) By producing air and ammonia gas separately, and then mixing the same in the proper proportions in a suitable mixing chamber. The mixing chamber may consist of an aluminium box with inlets for air and ammonia placed tangentially, and containing baffle plates.

(2) By producing directly a mixture of air and ammonia gas by passing a stream of air through aqueous ammonia in a suitable apparatus.

The second method is by far the better, and will alone be described.

The source of ammonia which may be considered in this connection is practically only purified ammonia liquor, containing 20 to 25 per cent. NH_3, "free from sulphur." This liquor is fed at the desired rate to an ammonia still, where it is met by low-pressure steam blown in at the bottom, either directly or through coils, and by a current of air. Ammonia gas is liberated, mixed with the right proportion of air for oxidation, and, if the top of the column is kept cool, the gas is fairly dry. Moisture has no influence on the oxidation, but is liable to condense in the filters and impair their efficiency. Iron pipes joined with red lead and oil may be used *before* the filters are reached, and lead or aluminium pipes after the filters, although lead or aluminium is preferable throughout.

In a type of apparatus designed by the United Alkali Company, the still is replaced by a tall coke tower. Steam and air are introduced as before, but the ammonia liquor is introduced at a point two-thirds the height of the tower. The upper portion of the tower then acts as a cooler and gas filter, and no further filtration is required.

The air is supplied from a blower under suitable pressure; this pressure will depend on the type of apparatus used for producing the ammonia, but should not fall below about 5 pounds per square inch. The air supplied to the converter should be pure and free from dust. After the blower there should be a trap to catch oil mechanically carried over. A suitable meter for the air is an orifice meter.

The filtering medium is glass-wool, free from dust; it may require to be renewed about once a month, so that a spare filter should be provided. If the ammonia gas is taken directly from the generator, and is therefore saturated with moisture, a steam coil may be introduced into the filter, if necessary, to prevent condensation.

The hot gases from the converter are conveyed through a lagged aluminium main or, after some cooling, through a pottery main, to the Glover tower, burner pipe, dust catcher, or other suitable point of entry, to the chamber plant. In this connection it is necessary to ensure—

(1) That the temperature always remains high enough to keep the water from condensing in the main, or other part of the system, where the nitric acid contained in the condensate is not utilised.

(2) That there is no pressure such as would cause burner gas to pass back through the converter in case of stoppage, or, if there is such a pressure, that a liquid seal trap is provided.

A suitable cooler consists of a battery of three silica S-pipes, 4 inches in diameter and 6 feet long, exposed to the free air.

One feature of the ammonia oxidation process is its very uniform working, and unless very special reasons make it impossible to run the chamber plant equally uniformly, it is desirable to take advantage of the uniformity in supply of oxides of nitrogen furnished by an ammonia oxidation converter. This applies more particularly when a mixture of air and ammonia of uniform composition is to be obtained in the apparatus described, which works very regularly when once adjusted, but would probably be somewhat troublesome if the rates of flow were constantly altered. If, however, it is found absolutely necessary to vary the supply of oxides of nitrogen within somewhat wide limits, there would be no difficulty in running the converter at 15 per cent. of its maximum output if the supply of ammonia could be suitably regulated.

The Economics of Nitric Acid Manufacture by the Oxidation of Ammonia.

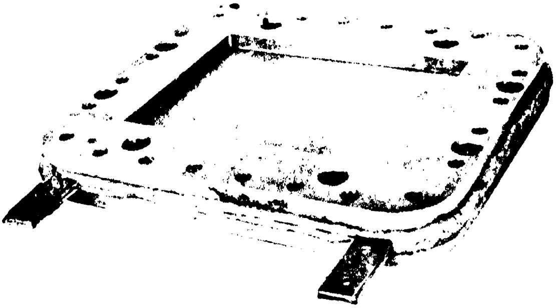
In consequence of the fact that large-scale ammonia oxidation plants have only been established during the war period, it is difficult to get reliable figures as to the costs involved in operating the process with modern types of plant. It may also be noted that these plants have been erected for the sole purpose of meeting military requirements, and questions as to economy in construction and operation have been matters of minor importance.

As previously stated, the process may be utilised for the production of dilute or concentrated nitric acid, and in considering the question of costs it is convenient to deal separately with the different sections constituting a complete factory—namely:

Converter and absorption (dilute acid) section.
Acid-concentrating section.
Ammonia-producing section.

The capital and working costs are therefore set out under separate headings below.

PLATE XIX



DOUBLE PLATINUM GAUZE CATALYST OF [illegible] TYPE

Two gauzes are used, separated by [illegible]. The lower one is electrically heated by silver lead[illegible]. The gauzes are clamped with asbestos and mica packing [illegible] the whole unit is then bolted into the converter [illegible] Plate XVIII.

Capital Cost of Converter and Absorption (Dilute Acid) Sections.

Several figures were published prior to the war concerning the cost of small ammonia oxidation factories for producing dilute nitric acid (53 per cent.), and indicate a capital cost of the order of £10 per ton of HNO_3 (calculated as 100 per cent.) per annum (*Iron and Coal Trades Review*, May 23, 1913; *Chemical Trade Journal*, March 7, 1914; *Die Chemische Industrie*, 1914, vol. xxxvii., p. 267).

A certain amount of additional information of more recent date has been collected by the Nitrogen Products Sub-Committee.

The principal items in the cost of an ammonia oxidation factory are represented by the absorption towers and by the converters and the initial supply of platinum, as was shown by the previous figures.

The evidence available to the Sub-Committee indicated that recourse need not be had to costly granite towers of the type used in connection with arc-furnace installations in Norway, and that stoneware towers of a much less expensive character can be employed. The utilisation of modern types of converter units having a large output, amounting to, say, 300 tons of HNO_3 (calculated as 100 per cent.) per annum, also leads to a substantial reduction in the cost both of the converter section itself and of the initial supply of platinum. Definite evidence based upon quotations at *war prices* is available on the latter points as the result of the research work carried out under the direction of the Experiments Sub-Committee.

The figures for cost given show a considerable variation. As the result, however, of a careful examination of all the evidence under review, the Sub-Committee is of the opinion that the capital cost of the converter and absorption-tower sections of a large-scale ammonia oxidation factory embodying the best modern features and having an annual output of dilute acid (53 per cent.) equivalent to, say, 10,000 tons of HNO_3 (calculated as 100 per cent.), should be of the order of £5 per metric ton of HNO_3 (calculated as 100 per cent.) per annum on the basis of pre-war conditions in this country.

This figure is equivalent to £22·5 per metric ton of combined nitrogen per annum, and has been provisionally adopted by the Sub-Committee. For the reasons previously specified, it must be regarded as of a tentative character.

In arriving at a conclusion as to the probable cost, the Nitrogen Products Committee took into account the capital cost of the concentrating section of an arc-furnace installation, £5 per metric ton of HNO_3 (calculated as 100 per cent.) per annum. The primary product of the arc process is a dilute acid of 30 to 40 per cent. strength, as against an acid of about 53 per cent. strength in the case of the ammonia oxidation process. The preliminary evaporating plant necessary in the case of the arc process for bringing the dilute acid to a strength of about 50 per cent. prior to treatment in the main concentrating plant will thus not be required in the case of the acid obtained by the oxidation of ammonia.

Taking this factor into account the Sub-Committee adopted a figure of £3 per metric ton of HNO_3 (calculated as 100 per cent.), or £13·5 per metric ton of combined nitrogen per annum for the capital cost of the concentrating section of an ammonia-oxidation factory of the scale of 10,000 tons of nitric acid per annum, on the basis of pre-war conditions in this country.

The total cost of the conversion, absorption, and concentrating sections of a large factory would thus amount to £8 per metric ton of HNO_3 (calculated as 100 per cent.) per annum, equivalent to £36 per metric ton of combined nitrogen per annum in the form of concentrated acid.

The probable capital costs of complete factories for producing dilute (50 to 53 per cent.) or concentrated (93 to 96 per cent.) nitric acid on a large scale are obtained by adding the figures previously adopted to the cost of an ammonia-producing plant.

It may be noted that an over-all efficiency of 90 per cent. has been taken in respect of the converter and absorption sections, thus necessitating an ammonia section having a capacity of 0·3 metric ton per unit capacity of the dilute nitric acid section of the factory. In the case of a factory for producing *concentrated* nitric acid, allowance has been made for a margin of 3 per cent. in the capacities of the ammonia

ESTIMATED CAPITAL COSTS OF NITRIC ACID FACTORIES.

Nature of Ammonia-producing Section of Nitric Acid Factory, and Cost thereof per Metric *Ton of NH_3 per Annum.*	£ *per* Metric *Ton per Annum.*			
	Factory for Dilute *Acid.*		*Factory for* Concentrated *Acid.*	
	HNO_3 (as 100 per Cent.).	*Combined Nitrogen.*	*HNO_3 (as 100 per Cent.).*	*Combined Nitrogen.*
By-product ammonia (plant for utilising)—	£	£	£	£
(*a*) Crude gasworks liquor (£12·0)	8·60	38·70	11·86	53·36
(*b*) Concentrated gas liquor (£8·0)	7·40	33·30	10·62	47·80
Cyanamide ammonia (installation for producing by *continuous* cyanamide process):				
(*a*) Complete carbide-cyanamide and ammonia sections with power section at £10·26 per kilowatt demanded (£44·50)	18·35	82·58	21·90	98·55
(*b*) Carbide-cyanamide and ammonia sections (*ex*-power section) (£26·88)	13·06	58·77	16·45	74·03
(*c*) Cyanamide conversion section only (cyanamide purchased) (£5·04)	6·51	29·30	9·70	43·67
Haber ammonia (installation for producing) (£40·0)	17·00	76·50	20·51	92·29

and dilute acid sections, in order to compensate for losses of combined nitrogen during the concentrating stage.

The Sub-Committee is of the opinion that the working costs of the converter and absorption sections of a large-scale ammonia-oxidation factory embodying the best modern features should not exceed £2 per metric ton of HNO_3 (calculated as 100 per cent.) in the form of dilute acid, or £9 per metric ton of combined nitrogen.

This figure represents the costs of conversion upon the basis of pre-war conditions in this country, and is inclusive of amortisation at the rate of 10 per cent. on the tentative capital cost previously adopted. It is exclusive, however, of interest on capital and of losses of ammonia during the conversion.

Cost of Concentrating Dilute Acid.—In consequence of the absence of any body of waste heat in the gases resulting from the oxidation of ammonia, the concentration of the dilute acid has to be effected by the employment of fuel. The costs are therefore likely to be somewhat greater than in the case of the arc process, although the dilute acid from the latter process is weaker than that obtained by the ammonia-oxidation process.

Taking into account the corresponding costs in the case of the arc process, the Sub-Committee considered that an allowance of £2·5 per metric ton of HNO_3 (calculated as 100 per cent.), including amortisation at 10 per cent., would be reasonable for a large-scale plant upon the basis of pre-war conditions.

The equivalent value per metric ton of combined nitrogen is £11·25, thus bringing the total working costs for oxidation and concentration to £20·25 per metric ton of combined nitrogen or £4·5 per metric ton of HNO_3 (calculated as 100 per cent.) in the form of strong acid, exclusive of interest on capital and of losses of ammonia.

The table on p. 305 indicates, in a comparative manner, the estimated costs of manufacturing dilute and concentrated nitric acid on a large scale from synthetic and by-product ammonia on the basis of pre-war conditions.

In the case of synthetic ammonia, the figures represent the *estimated manufacturing costs* inclusive of losses.

ESTIMATED PRODUCTION COSTS OF NITRIC ACID.

Source of Ammonia and Cost thereof in £ per Metric Ton	£ *per* Metric *Ton.*			
	Dilute Acid.		*Concentrated* Acid.	
	HNO_3 *(as* 100 *per Cent.).*	*Combined Nitrogen.*	HNO_3 *(as* 100 *per Cent.).*	*Combined Nitrogen.*
By-product ammonia (market prices):				
(*a*) Pre-war (average 1911-1913) sulphate basis for crude liquor, with allowances for loss and for purification (£49·78) ..	16·93	76·19	19·94	89·72
(*b*) Lowest known sulphate basis for crude liquor, with allowances for loss and for purification (£24·52)	9·36	42·12	12·14	54·63
Cyanamide ammonia (estimated costs by *continuous* cyanamide process):				
With energy at—				
(*a*) £3·75 per kilowatt-year (£24·18)	9·25	41·62	12·03	54·12
(*b*) £3·0 ,, ,, (£22·89)	8·87	39·91	11·63	52·36
(*c*) £2·0 ,, ,, (£21·18)	8·35	37·57	11·10	49·95
(*d*) £1·2 ,, ,, (£19·79)	7·94	35·73	10·68	48·05
Haber ammonia (estimated costs):				
(*a*) "Probable" (£17·00)	7·10	31·95	9·81	44·15
(*b*) Tentative (£15·57)	6·67	30·01	9·37	42·16

Note.—The figures given above represent the estimated factory costs of the products, inclusive of all working expenses, of amortisation, and losses of combined nitrogen. They are exclusive, however, of any allowance for interest on the capital cost of the chemical installations.

In the case of by-product ammonia, the figures have been derived from the *pre-war market value of sulphate,* and an allowance of £7 per metric ton of ammonia has been added for the cost of concentration and purification. Account has also been taken of the loss of ammonia, amounting to 5 per cent., during the working up of the crude liquor.

The over-all efficiency of the conversion and absorption sections has been taken at 90 per cent., involving the employment of 0·3 metric ton of ammonia per metric ton of HNO_3 (calculated as 100 per cent.) produced. Account has also been taken of the loss of ammonia, amounting to 5 per cent., during the working up of the crude liquor.

The cost of manufacturing concentrated (90 per cent.) nitric acid in this country from Chile nitrate by the retort process amounted to about £22·33 per metric ton of HNO_3 (calculated as 100 per cent.) under pre-war conditions.

The Manufacture of Synthetic Nitrates.

A brief indication will be given of the manufacture of nitrates, such as calcium nitrate and sodium nitrate, from the dilute acid obtained by the oxidation of ammonia. For this purpose use will be made of the relevant figures dealing with the manufacture of nitrates by means of the arc process.

The plant required for the conversion of dilute acid into calcium nitrate (13 per cent. N) and for packing the product entails a capital outlay of £22·55 per metric ton of combined nitrogen per annum, or £2·93 per metric ton of nitrate (13 per cent. N) per annum, for a large-scale installation.

The capital outlay would probably be somewhat lower in connection with the manufacture of sodium nitrate, owing to the packing installation being of a less elaborate character.

The following table indicates the probable over-all capital costs of large-scale factories for manufacturing *calcium nitrate* by ammonia oxidation. The figures are obtained by adding the capital cost of a nitrate section per metric ton of combined nitrogen per annum to the corresponding capital costs of factories for producing dilute nitric acid as given. No allowance has been made for the small loss of combined nitrogen involved in the conversion of the dilute acid into nitrate.

ESTIMATED CAPITAL COSTS OF CALCIUM NITRATE FACTORIES.

Nature of Ammonia-Producing Section of Calcium Nitrate Factory.	£ *per* Metric *Ton per Annum.*	
	Nitrate (13 *per Cent. Nitrogen*).	*Combined Nitrogen.*
By-product ammonia (plant for utilising)—	£	£
(*a*) Crude liquor	7·96	**61·25**
(*b*) Concentrated liquor	7·26	**55·85**
Cyanamide ammonia (installation for producing by *continuous* cyanamide process)—		
(*a*) Complete carbide-cyanamide and ammonia sections with power section at £10·26 per kilowatt demanded	13·67	**105·13**
(*b*) Carbide-cyanamide and ammonia sections (*ex*-power section)	10·57	**81·33**
(*c*) Cyanamide conversion section only (cyanamide purchased)	6·74	51·85
Haber ammonia (installation for producing) ..	12·87	**99·05**

Owing to the lack of any body of waste heat from the gaseous products of the ammonia-oxidation process, the evaporation of the nitrate solutions will have to be effected largely by the use of fuel.* The dilute acid has a strength of about 53 per cent., so that approximately 1 ton of water has to be evaporated for every ton of HNO_3 (calculated as 100 per cent.) neutralised. Assuming the use of open evaporating-pans, the fuel requirements will amount to about 0·17 ton, and the cost, with fuel at £0·5 per ton, to £0·085 per ton of HNO_3 (calculated as 100 per cent.) neutralised. If vacuum evaporating-pans were employed, the fuel requirements would be substantially lower.

If allowance is made for a loss of combined nitrogen amounting to about 2·5 per cent. during the conversion of dilute acid into calcium nitrate, every metric ton of HNO_3 (calculated as 100 per cent.) neutralised yields 1·67 metric tons of nitrate (13 per cent. N). The charges for lime and limestone (£0·202) and for casks for packing the product (£1·25) will be the same as in the case of the arc process, but an increased allowance of, say, £0·75 per metric ton of nitrate must be made in respect of labour, repairs, expenses, and depreciation, on account of the extra labour entailed by the use of fuel for evaporating purposes. Taking into account the cost of the fuel (£0·085 per ton of HNO_3 neutralised), the total working costs amount to £2·253 per metric ton of calcium nitrate (13 per cent. N).

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* See, however, reference on p. 277.

The table given on p. 309 indicates the estimated production costs at large-scale nitrate factories comprising ammonia-oxidation sections for manufacturing the dilute nitric acid.

Sodium Nitrate.—Allowing for a loss of about 2·5 per cent. as before, every metric ton of HNO_3 (calculated as 100 per cent.) neutralised will yield 1·39 metric tons of sodium nitrate (15·6 per cent. N). The charges for soda ash at £3 per ton (£1·815) and for bags (£0·25) will be the same as in the case of the arc process, and an increased allowance of £0·75 per metric ton of nitrate will be taken, as before, for labour, repairs, expenses, and depreciation. Taking account of the cost of fuel (£0·085 per metric ton of HNO_3 neutralised), the total working expenses amount to £2·876 per metric ton of sodium nitrate (15·6 per cent. N).

The *pre-war market price* of calcium nitrate in this country amounted to £9·75 per long ton, or £9·59 per metric ton, equivalent in the case of a nitrogen content of 13 per cent. to £73·8 per metric ton of combined nitrogen.

The *pre-war market price* (average 1911-1913) of Chile nitrate amounted to £10·52 per metric ton, or £67·21 per metric ton of combined nitrogen.

Ammonium Nitrate, NH_4NO_3.

Prior to the war the manufacture of ammonium nitrate was carried out only on a comparatively small scale, on account of the limited applications of the material to industrial purposes. Considerable attention has been given to the possibility of utilising ammonium nitrate as a fertiliser on account of its high content of nitrogen (35 per cent.), and the consequent economy in packing and transport. The endeavours hitherto made in this direction however, have not wholly succeeded in

ESTIMATED PRODUCTION COSTS OF CALCIUM AND SODIUM NITRATES.

Source of Ammonia, and Cost of Dilute Nitric Acid obtained therefrom in £ per Metric *Ton of HNO_3.*	*Packed product, £ per* Metric *Ton.*			
	Nitrate.		*Combined Nitrogen.*	
	Calcium (13 *per Cent. N*).	*Sodium* (15·6 *per Cent. N*).	*As Calcium Nitrate.*	*As Sodium Nitrate.*
By-product ammonia (market prices):				
(*a*) Pre-war (average 1911-1913) sulphate basis (£16·93) ..	12·39	15·45	95·31	96·50
(*b*) Lowest known sulphate basis (£9·36)	7·86	9·61	60·45	61·60
Cyanamide ammonia (estimated cost by *continuous* cyanamide process):				
With energy at—				
(*a*) £3·75 per kilowatt-year (£9·25)	7·79	9·53	59·92	61·09
(*b*) £3·0 ,, ,, (£8·87)	7·56	9·26	58·15	59·34
(*c*) £2·0 ,, ,, (£8·35)	7·25	8·88	55·77	56·94
(*d*) £1·2 ,, ,, (£7·94)	7·01	8·59	53·92	55·05
Haber ammonia (estimated cost):				
(*a*) "Probable" (£7·10)	6·50	7·98	50·00	51·18
(*b*) Tentative (£6·67)	6·25	7·67	48·08	49·19

Note.—The figures given above represent the estimated factory costs of the *packed* product, inclusive of all working expenses, of amortisation, and of losses of combined nitrogen. They are exclusive, however, of any allowance for interest on the capital cost of the chemical installations overcoming the drawbacks due to the solubility and deliquescent properties of the nitrate.

As a direct outcome of the enormous demand for explosives under war conditions and of the limitations governing the manufacture of trinitro-toluene, the ammonium nitrate industry assumed a position of outstanding importance during the war period. The high-explosive shells used by the British Army were filled with a mixture of 80 parts of ammonium nitrate and 20 parts of trinitro-toluene (T.N.T.).

The normal method of making the nitrate by the neutralisation of dilute nitric acid with ammonia was found to be unsuitable for coping with the demand, and other methods dispensing with the necessity for the preliminary manufacture of nitric acid were therefore resorted to. From the economic aspect some of the new processes can only be regarded as war emergency measures.

The following is a brief summary of the various methods of manufacture that have been employed in this country:

By Direct Union of Ammonia and Nitric Acid.—For this method the dilute acid obtained by means of the arc process or the ammonia-oxidation process is well adapted. If by-product ammonia is employed, it must be freed from sulphur and pyridene, and other impurities, in order that the resulting ammonium nitrate may be sufficiently stable for explosives purposes.

The process is a simple one, but the corrosive action of the nitrate solution upon most metals leads to heavy wear and tear of the evaporating-pans. To prevent rapid corrosion of the iron pans, a slight excess of ammonia had to be maintained in the liquid, leading to loss by volatilisation.

A modification of the process was devised whereby the necessity for evaporation is avoided. Gaseous ammonia is passed into strong nitric acid under such conditions that neutral ammonium nitrate is formed, the heat of reaction driving off practically all the water and melting the solid product, which can be run off and allowed to solidify. The pan corrosion is heavy, and the process is attended with appreciable loss.

By the Interaction of Calcium Nitrate and Ammonium Car-

bonate.—This reaction proceeds readily, the purity of the resulting ammonium nitrate depending upon that of the original calcium nitrate. The latter can be obtained by the neutralisation of dilute acid with limestone, as in the arc process, or by the double decomposition of Chile nitrate and calcium chloride:

$$2NaNO_3 + CaCl_2 \rightleftarrows Ca(NO_3)_2 + 2NaCl \text{ (precipitate).}$$

By Modification of the Ammonia-Soda Process.—The ordinary ammonia-soda process (p. 170) is modified by substituting Chile nitrate for sodium chloride, the ammonium nitrate being separated from the liquor by evaporation after the removal of the sodium bicarbonate. Technical difficulties have been encountered in connection with the conversion ratio of Chile nitrate to ammonium nitrate, in the separation of the latter from the sodium bicarbonate, and owing to the accumulation of impurities in the mother liquor.

By the Interaction of Chile Nitrate and Ammonium Sulphate: $2NaNO_3 + (NH_4)_2SO_4 = 2NH_4NO_3 + Na_2SO_4$.—The successful development of this method of manufacturing ammonium nitrate by double decomposition was accomplished after a detailed examination of the solubilities of the reaction products and of the temperatures necessary to prevent the formation of double salts. It may be noted that the process involves the loss of sulphuric acid, which goes to waste in the form of sodium sulphate.

The new methods described above involve, in general, reactions which proceed to an equilibrium, thus resulting in losses of the combined nitrogen of the initial reagent, and also leading to difficulty in the separation of ammonium nitrate of the requisite degree of purity.

The Economics of Ammonium Nitrate Manufacture.—In dealing with the question of costs, it is convenient to remember that ammonium nitrate contains ammonia nitrogen and nitric nitrogen in equal proportions. The cost of a ton of combined nitrogen in the form of ammonium nitrate is therefore equivalent to the added costs of half a ton of combined nitrogen in the form of ammonia, and of half a ton in the form of dilute nitric acid, together with the cost of neutralising, evaporating, etc., and with an allowance for losses during the process.

In considering the probable cost of a large-scale nitrate plant upon the basis of pre-war conditions in this country, account has been taken of the fact that the manufacture of ammonium nitrate was a minor industry prior to the war. The Sub-Committee is of the opinion that a figure of £7 per metric ton of combined nitrogen per annum, or £2·45 per metric ton of ammonium nitrate per annum, should be adequate for the pre-war capital cost of a large-scale ammonium nitrate section, including provision for storage of a certain amount of ammonia.

It is obvious that many variations are possible in respect of the nitric acid and ammonia sections of a complete ammonium nitrate factory. For example, the nitric acid may be obtained from Chile nitrate plant, an arc-furnace installation, or an ammonia-oxidation plant, while the ammonia may be synthetic or may be obtained from by-product sources or from cyanamide.

The table on p. 313 deals with a few of the more important variations, and indicates, in a comparative manner, the probable order of the over-all capital costs of large-scale factories on the basis of pre-war conditions. It has been assumed that ammonium nitrate of a high degree of purity would be manufactured, thus involving the use of purification plant for the ammonia when the by-product source is relied upon.

The figures indicate that the capital outlay is large in the case of all the purely synthetic processes. In the case of an ammonia-oxidation plant utilising by-product ammonia or provided with a cyanamide conversion section only, the capital costs are much lower, and are on a parity with those incurred if ammonium nitrate is manufactured from Chile nitrate and by-product ammonia. In the two latter cases no account is taken of the capital necessary to *produce* the Chile nitrate or the by-product ammonia.

The neutralisation process is a comparatively simple one, and, judging by analogy with other manufacturing operations of a similar character, the conversion costs should not be very large, apart from the question of repairs. The latter item is likely to be fairly heavy, on account of the corrosive action of

ESTIMATED CAPITAL COSTS OF AMMONIUM NITRATE FACTORIES.

Type of Nitric Acid Section and Capital Cost thereof in £ per Metric *Ton of Combined Nitrogen per Annum.*	*Type of Ammonia Section and Capital Cost thereof in £ per* Metric *Ton of Combined Nitrogen per Annum.*	*Over-all Capital Cost (£ per* Metric *Ton per Annum).*	
		Combined Nitrogen.	*Ammonium Nitrate (35 per Cent. Nitrogen).*
		£	£
Arc furnace installation comprising chemical section and power section at £10·26 per kilowatt demanded (£156·04).	(*a*) *By-product ammonia:* plant for *concentrated* liquor (£9·71)	89·87	31·45
	(*b*) *Cyanamide ammonia:* conversion plant only (£6·12)	88·08	30·83
Ammonia oxidation installation: (*a*) With by-product ammonia section; plant for *concentrated liquor* (£33·30).	(*a*) *By-product ammonia:* plant for *concentrated* liquor (£9·71)	28·50	9·97
(*b*) With cyanamide ammonia section (*continuous* cyanamide process); complete carbide-cyanamide and ammonia factory with power section at £10·26 per kilowatt demanded (£82·58).	(*b*) *Cyanamide-ammonia* section (*continuous* cyanamide process); complete carbide-cyanamide and ammonia factory with power section at £10·26 per kilowatt demanded (£54·03) ..	75·30	26·35
(*c*) With cyanamide conversion plant only (£29·30).	(*c*) Cyanamide conversion plant only (£6·12) ..	24·71	8·65
(*d*) With Haber ammonia section (£76·50).	(*d*) *Haber ammonia* plant (£48·56)	69·53	24·33
Chile nitrate plant with sulphuric acid section (£27·67).	*By-product ammonia:* plant for *concentrated* liquor (£9·71)	25·69	8·99

the solution on the evaporating-pans. As the result of a careful examination of all the evidence available, the Nitrogen Products Sub-Committee adopted the figure of £1·65 per metric ton of ammonium nitrate as likely to be incurred under pre-war conditions in the working of a large-scale plant. The figure is equivalent to £4·71 per metric ton of combined nitrogen, and has been taken as *exclusive* of any allowance for losses of combined nitrogen during the conversion, or of interest on capital.

The employment of fuel would be unnecessary in the case of the manufacture of ammonium nitrate at an arc-furnace installation, as the waste heat from the furnace gases would more than suffice for evaporating purposes. The saving effected would probably reduce the cost of conversion to about £1·5 per metric ton of nitrate, or £4·28 per metric ton of combined nitrogen. This tentative figure is utilised below in dealing with the over-all production costs at an arc-process plant.

The table on p. 315 is on the lines of that given previously in connection with capital costs, and serves to illustrate the probable order of the over-all production costs at large-scale ammonium nitrate factories.

According to the evidence available, the losses of combined nitrogen during the neutralisation process are not very large, but an allowance of 2·5 per cent. has been included in the figures given below. It has been assumed that a pure product is manufactured, thus involving a charge for the purification of by-product ammonia when this source is relied upon.

It is interesting to observe that processes depending upon the use of Chile nitrate or by-product ammonia are characterised by the highest production costs and compare unfavourably with the purely synthetic processes. The influence of cheap ammonia from which cheap nitric acid can be obtained by means of the ammonia-oxidation process is shown to a marked degree.

The *pre-war market price* of ammonium nitrate amounted to £35·75 per long ton, equivalent to £35·18 per metric ton, or £100·5 per metric ton of combined nitrogen.

ESTIMATED PRODUCTION COSTS OF AMMONIUM NITRATE BY NEUTRALISATION PROCESS.

Source of Dilute Nitric Acid and Cost thereof in £ per Metric Ton of Combined Nitrogen.	*Source of Ammonia and Cost thereof in £ per Metric Ton of Combined Nitrogen.*	*Over-all Production Costs, £ per Metric Ton*	
		Combined Nitrogen.	*Ammonium Nitrate (35 per Cent Nitrogen).*
From arc furnace installation : With energy at—	*By-product ammonia* : cost of crude liquor on basis of pre-war sulphate (average 1911-1913), with allowances for loss and for purification (£60·42).		
(*a*) £3·75 per kilowatt-year (£42·80)		57·18	20·01
(*b*) £3·0 ,, (£36·50)		53·95	18·88
(*c*) £2·0 ,, (£28·08)		49·63	17·37
(*d*) £1·2 ,, (£21·35)		46·18	16·16
From ammonia oxidation installation : (*a*) Using by-product ammonia: cost of crude liquor on basis of pre-war sulphate.	(*a*) *By-product ammonia* ; cost of crude liquor on basis of pre-war sulphate, with allowances for loss and for purification:		
(i.) Average, 1911-1913 (£76·19)	(i.) Average 1911-1913 (£60·42)	74·72	26·15
(ii.) Lowest known (£42·12)	(ii.) Lowest known (£29·77)	41·55	14·54
(*b*) Using cyanamide ammonia (*continuous cyanamide process*): With energy at—	(*b*) *Cyanamide ammonia* (continuous cyanamide process): With energy at—		
(i.) £3·75 per kilowatt-year (£41·62)	(i.) £3·75 per kilowatt-year (£29·36)	41·09	14·38
(ii.) £3·0 ,, (£39·91)	(ii.) £3·0 ,, (£27·79)	39·40	13·79
(iii.) £2·0 ,, (£37·57)	(iii.) £2·0 ,, (£25·70)	37·13	12·99
(iv.) £1·2 ,, (£35·73)	(iv.) £1·2 ,, (£24·03)	35·34	12·37
(*c*) Using Haber ammonia:	(*c*) *Haber ammonia* :		
(i.) "Probable" (£31·95)	(i.) "Probable" (£20·64)	31·66	11·08
(ii.) Tentative (£30·01)	(ii.) Tentative (£18·90)	29·77	10·42
From Chile nitrate : weak acid (65 per cent.) at £14 per long ton. pre-war (£95·38)	*By product ammonia* : cost of crude liquor on basis of pre-war sulphate (average 1911-1913). with allowances for loss and for purification (£60·42)	84·56	29·59

Note.—The figures given above represent the estimated factory costs of the product inclusive of all working expenses, of amortisation, and of losses of combined nitrogen. They are exclusive, however, of any allowance for interest on the capital costs of the chemical installations.

PRODUCTION COSTS OF NITROGEN COMPOUNDS: FACTORY SPECIFIED, EXCLUSIVE OF ROYALTIES AND LIKE NITROGEN IN

Initial Process or Product (with Explanatory Notes).	
By-Product Ammonia:	
Col. (1). Market value. Value of *crude* liquor based on value of sulphate with allowance for added *market value* of pure ammonia spirit.	Based on pre-war (average 1911-1913) market value
,, (2). Market value.	
,, (4), (5), (6), (7), (8). Via ammonia-oxidation process; value of *crude* liquor as in (1), with allowance for *cost* of purification. In the case of synthetic sodium nitrate (Col. 7), soda ash is taken at £3 per metric ton.	Based on lowest known market value (1897) ..
Haber Process:	
Col. (4), (5), (6), (7), (8). Via ammonia-oxidation process. In the case of synthetic sodium nitrate (Col. 7), soda ash is taken at £3 per metric ton.	"Probable" .. .. .. Tentative .. .. ..
Cyanamide Process (Continuous):	
Col. (1), (2). Inclusive of cost of carbide-cyanamide stages.	With power (steam-generated) at £3·75 per kilowatt-year .. ..
,, (3). Raw cyanamide, unpacked and exclusive of cost of after-treatment.	With power at £3·0 per kilowatt-year .. ..
,, (4), (5), (6), (7), (8). Via ammonia-oxidation process, including cost of carbide, cyanamide, and ammonia stages. In the case of synthetic sodium nitrate (Col. 7), soda ash is taken at £3 per metric ton.	With water power at £2·0 per kilowatt-year .. With water power at £1·2 per kilowatt-year ..
Arc Process:	
Col. (6), (7), (8). Inclusive of cost of producing dilute nitric acid. In the case of synthetic sodium nitrate (Col. 7), soda ash is taken at £3 per metric ton.	With power (steam generated) at £3·75 per kilowatt-year .. .. With power at £3·0 per kilowatt-year .. ..
,, (8). Value of by-product ammonia used for neutralisation based on market value of sulphate (average 1911-1913), with allowance for *cost* of purifying concentrated ammonia liquor.	With water power at £2·0 per kilowatt-year .. With water power at £1·2 per kilowatt-year ..
Chile Nitrate:	
Col. (5). Factory costs in United Kingdom based on market value of Chile nitrate.	Based on pre-war (average 1911-1913) market value
,, (7). Market value.	
,, (8). Inclusive of cost of dilute acid and of by-product ammonia for neutralisation. Value of ammonia as under Arc process (Col. 8).	Based on "lowest possible" market value .. .. Based on war conditions, market value in 1916 ..

COSTS OF UNPACKED PRODUCTS UNLESS OTHERWISE
PAYMENTS (£ PER METRIC TON OF COMBINED
FORM SPECIFIED).

1. Pure Ammonia as Liquor (20–25 per Cent. NH_3).	2. Ammonium Sulphate (25 per Cent. NH_3) (Packed).	3. Calcium Cyanamide (19–19·5 per Cent. N) (Raw).	4. Nitric Acid (Dilute).	5. Nitric Acid (Concentrated).	6. Calcium Nitrate (13 per Cent. N) (Packed).	7. Sodium Nitrate (15·6–15·65 per Cent. N) (Packed).	8. Ammonium Nitrate (35 per Cent. N) (Unpacked
61·59	66·10	—	76·19	89·72	95·31	96·50	74·72
32·40	35·84	—	42·12	54·63	60·45	61·60	41·55
20·84	29·29	—	31·95	44·15	50·00	51·18	31·66
18·90	27·55	—	30·01	42·16	48·08	49·19	29·77
29·36	38·01	24·04	41·62	54·12	59·92	61·09	41·09
27·79	36·44	22·56	39·91	52·36	58·15	59·34	39·40
25·71	34·36	20·59	37·57	49·95	55·77	56·94	37·13
24·03	32·68	19·01	35·73	48·05	53·92	55·05	35·34
—	—	—	42·80	51·80	58·83	60·31	57·18
—	—	—	36·50	45·50	52·37	53·84	53·95
—	—	—	28·08	37·08	43·76	45·22	49·63
—	—	—	21·35	30·35	36·86	38·32	46·18
—	—	—	—	100·48	—	67·21	84·56
—	—	—	—	75·98	—	44·02	—
—	—	—	—	132·84	—	100·87	—

PRODUCTION COSTS OF NITROGEN COMPOUNDS: FACTORY SPECIFIED, EXCLUSIVE OF ROYALTIES AND LIKE IN FORM

Initial Process or Product (with Explanatory Notes).	
By-Product Ammonia:	
Col. (1). Market value. Value of *crude* liquor based on value of sulphate with allowance for added *market value* of pure ammonia spirit.	Based on pre-war (average 1911-1913) market value
„ (2). Market value.	
„ (4), (5), (6), (7), (8). Via ammonia-oxidation process; value of *crude* liquor as in (1), with allowance for *cost* of purification. In the case of synthetic sodium nitrate (Col. 7), soda ash is taken at £3 per metric ton.	Based on lowest known market value (1897) ..
Haber Process:	
Col. (4), (5), (6), (7), (8). Via ammonia-oxidation process. In the case of synthetic sodium nitrate (Col. 7), soda ash is taken at £3 per metric ton.	"Probable" .. .. Tentative .. .. ..
Cyanamide Process (Continuous):	
Col. (1), (2). Inclusive of cost of carbide-cyanamide stages.	With power (steam-generated) at £3·75 per kilowatt-year .. ..
„ (3). Raw cyanamide. Extra cost of after-treatment and packing amounts to about £0·75 per ton.	With power at £3·0 per kilowatt-year .. ..
„ (4), (5), (6), (7), (8). Via ammonia-oxidation process, including cost of carbide, cyanamide, and ammonia stages. In the case of synthetic sodium nitrate (Col. 7), soda ash is taken at £3 per metric ton.	With water power at £2·0 per kilowatt-year .. With water power at £1·2 per kilowatt-year ..
Arc Process:	
Col. (6), (7), (8). Inclusive of cost of producing dilute nitric acid. In the case of synthetic sodium nitrate (Col. 7), soda ash is taken at £3 per metric ton.	With power (steam-generated) at (£3·75 per kilowatt-year .. .. With power at £3·0 per kilowatt-year .. ..
„ (8). Value of by-product ammonia used for neutralisation based on market value of sulphate (average 1911-1913) with allowance for *cost* of purifying concentrated ammonia liquor.	With water power at £2·0 per kilowatt-year .. With water power at £1·2 per kilowatt-year ..
Chile Nitrate:	
Col. (5). Factory costs in United Kingdom based on market value of Chile nitrate.	Based on pre-war (average 1911-1913) market value
„ (7). Market value.	
„ (8). Inclusive of cost of dilute acid and of by-product ammonia for neutralisation. Value of ammonia as under Arc process (Col. 8).	Based on "lowest possible" market value .. .. Based on war conditions, market value in 1916 ..

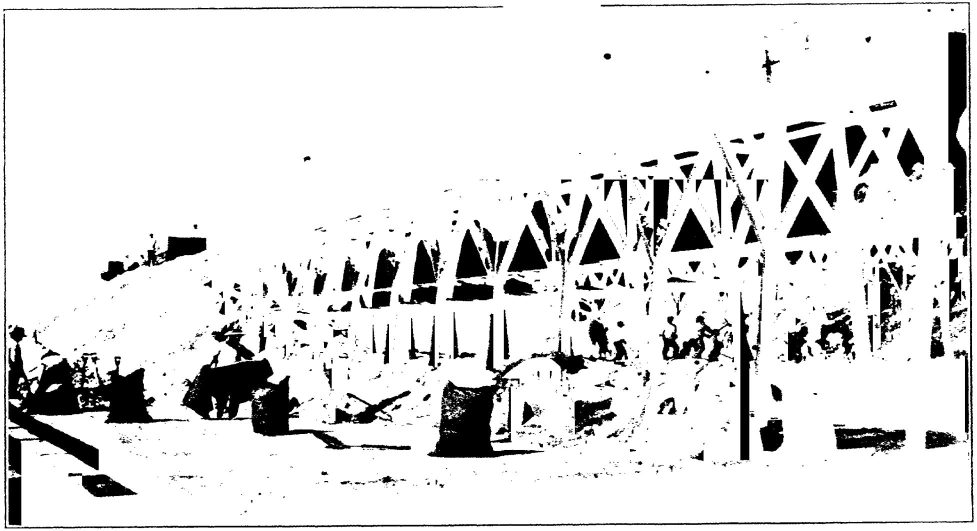
COSTS OF UNPACKED PRODUCTS UNLESS OTHERWISE PAYMENTS (£ PER METRIC TON OF PRODUCT SPECIFIED).

1. Pure Ammonia (calculated as 100 per Cent.) as Liquor (20–25 per Cent. NH_3).	2. Ammonium Sulphate (25 per Cent. NH_3) (Packed).	3. Calcium Cyanamide (19·5 per Cent. N) (Raw).	4. HNO_3 (calculated as 100 per Cent.) as Dilute Acid.	5. HNO_3 (calculated as 100 per Cent.) as Concentrated Acid.	6. Calcium Nitrate (13 per Cent. N) (Packed).	7. Sodium Nitrate (15·6–15·65 per Cent. N) (Packed).	8. Ammonium Nitrate (35 per Cent. N) (Unpacked).
50·74	13·61	—	16·93	19·94	12·39	15·05	26·15
26·69	7·38	—	9·36	12·14	7·86	9·61	14·54
17·00	6·03	—	7·10	9·81	6·50	7·98	11·08
15·57	5·67	—	6·67	9·37	6·25	7·67	10·42
24·18	7·83	4·69	9·25	12·03	7·79	9·53	14·38
22·89	7·50	4·40	8·87	11·63	7·56	9·26	13·79
21·18	7·07	4·01	8·35	11·10	7·25	8·88	12·99
19·79	6·73	3·71	7·94	10·68	7·01	8·59	12·37
—	—	—	9·51	11·51	7·65	9·41	20·01
—	—	—	8·11	10·11	6·81	8·40	18·88
—	—	—	6·24	8·24	5·69	7·05	17·37
—	—	—	4·74	6·74	4·79	5·98	16·16
—	—	—	—	22·33	—	9·52	29·59
—	—	—	—	16·88	—	6·89	—
—	—	—	—	29·52	—	—	—

CAPITAL EXPENDITURE FOR OPERATING NITROGEN FIXATION
LIKE PAYMENTS (£ PER METRIC TON OF COMBINED

Initial Process or Product (with Explanatory Notes).	
By-Product Ammonia:	
Col. (1). Plant for concentrating and/or purifying.	Utilising *crude* gasworks liquor .. .. ..
,, (2). Plant for fixing pure strong ammonia, with sulphuric acid section.	
,, (4), (5). As in (1) with ammonia-oxidation plant.	Utilising *concentrated* gas liquor .. .. ..
,, (6), (8). As in (4) with nitrate section.	
Haber Process:	
Col. (1). Ammonia factory including hydrogen and nitrogen sections.	
,, (2). As in (1) with fixing plant including sulphuric acid section.	
,, (4), (5). As in (1) with ammonia-oxidation section.	"Probable" cost ..
,, (6), (8). As in (4) with nitrate section.	
Cyanamide Process (Continuous):	
Col. (1). Complete with carbide-cyanamide, ammonia conversion, and steam power sections.	
,, (2). As in (1) with fixing plant including sulphuric acid section.	Chemical section only ..
,, (3). Complete with carbide-cyanamide and steam power sections.	Steam power section only at £10·26 per kilowatt demanded .. ..
,, (4), (5). As in (1) with ammonia-oxidation section.	
,, (6), (8). As in (4) with nitrate section.	Total .. ..
Arc Process:	
Col. (6), (8). As in (4) with nitrate section.	
,, (8). With addition of plant for preparing pure ammonia from *concentrated* gas liquor.	Chemical section only .. Steam power section only at £10·26 per kilowatt demanded .. ..
	Total .. ..
Chile Nitrate:	
Col. (7). Factory and nitrate grounds in Chile, including shipping for marketing product in Europe.	Factory in United Kingdom .. .. ..
,, (8). Nitric acid factory in United Kingdom, with sulphuric acid section and plant for preparing pure ammonia from *concentrated* gas liquor.	Factory and nitrate grounds in Chile, including shipping for marketing .. ..
	Total .. ..

PLATE [illegible]



DRYING FLOORS.

To face p. 50.

AND RECOVERY PROCESSES, EXCLUSIVE OF ROYALTIES AND NITROGEN PER ANNUM IN FORM SPECIFIED).

1. Pure Ammonia as Liquor.	2. Ammonium Sulphate.	3. Calcium Cyanamide.	4. Nitric Acid (Dilute).	5. Nitric Acid (Concentrated).	6. Calcium Nitrate.	7. Sodium Nitrate.	8. Ammonium Nitrate.
14·57	—	—	38·70	53·36	61·25	—	33·63
—	14·68	—	—	—	—	—	—
9·7	—	—	33·30	47·80	55·85	—	28·50
48·56	63·19	—	76·50	92·29	99·05	—	69·53
32·63	47·26	25·25	58·78	74·03	81·33	—	52·70
21·40	21·40	20·20	23·80	24·52	23·80	—	22·60
54·03	68·66	45·45	82·58	98·55	105·13	—	75·30
—	—	—	69·75	92·25	92·30	—	46·73
—	—	—	86·29	86·29	86·29	—	43·14
—	—	—	156·04	178·54	178·59	—	89·87
—	—	—	—	27·67	—	—	25·69
—	—	—	—	104·93	—	94·31	—
—	—	—	—	132·60	—	94·31	25·69

Direct Production of Nitrates.

The normal method of production of the nitrates of calcium, sodium, and ammonium in connection with an ammonia-oxidation plant is to obtain dilute nitric acid (55 per cent.) by absorption of the converter gas in towers in the usual way, and then to neutralise this acid by limestone, soda ash, or ammonia in the manner already described. This mode of procedure, however, obviously involves the use of expensive and bulky tower and neutralisation plant. In particular, the tower plant is the heaviest item in the cost of the nitric acid plant from ammonia oxidation.

The ideal method would be to make use of the converter gas directly, without resorting to the preliminary production of nitric acid. As the result of numerous experiments made by the authors, in conjunction with Mr. T. K. Brownson, it was found possible to produce nitrates directly from converter gas, limestone (or lime), soda ash, or ammonia. The methods are different in the case of calcium and sodium nitrates and ammonium nitrate, and will be dealt with separately.

The gas containing oxides of nitrogen, whether from arc furnaces (2 per cent. of nitric oxide) or from ammonia oxidation (about 10 per cent. of nitric oxide), are cooled and oxidised in the usual way with excess of air. If the gas is now passed through a series of absorbers containing milk of lime, a suspension of limestone, or a solution of caustic soda or sodium carbonate, the following reactions occur:

(1) In the first absorber, into which the gases enter, the whole or nearly the whole of the oxides of nitrogen is absorbed, with the formation of a mixture of nitrate and nitrite:

$$2NaOH+2NO_2=NaNO_3+NaNO_2+H_2O. \qquad (1)$$

During this stage of the process very little unabsorbed oxides of nitrogen pass to the later absorbers in the series, and it is there absorbed in the manner just described.

(2) When all the free alkali or limestone has been neutralised in the above manner, the oxides of nitrogen begin to be absorbed mainly as nitric acid. The nitric acid, however,

decomposes the nitrite in solution, with evolution of oxides of nitrogen, and the nitrite is converted into nitrate:

(i.) $2NO_2+H_2O=HNO_3+HNO_2$.
(ii.) $2HNO_2=H_2O+NO+NO_2$.
(iii.) $2NaNO_2+2HNO_3=2NaNO_3+H_2O+NO+NO_2$.
(iv.) $2NO+O_2=2NO_2$.

The gas containing NO_2 passes to the second absorber, and is there absorbed in accordance with equation I. When all the nitrite is decomposed, the first absorber is cut out of the series and the solution of nitrate run off for evaporation or other treatment. It was found that very concentrated solutions, which commenced to crystallise spontaneously, could be obtained, since the nitrates of calcium and sodium are very soluble in water. The evaporation will therefore be as economical as possible.

The first absorber is now charged with fresh alkali and put at the end of the series. The second absorber now functions in the same way as the first, and goes through all the reactions described. The process is therefore practically continuous.

Attempts were made to produce ammonium nitrate in the same way, using solutions of ammonia and ammonium carbonate, but without success. There were large losses of nitrogen. Another method had therefore to be adopted in this case. Working in conjunction with Mr. G. J. Jones, the writers found that dry, solid ammonium nitrate, perfectly free from nitrite, can be obtained by blowing a mixture of air, oxides of nitrogen, and a regulated amount of water vapour, such as is produced by cooling and suitably treating converter gas from the oxidation of ammonia, into a large chamber, and introducing into this atmosphere jets of ammonia gas. The ammonium nitrate is at once formed, and settles out at the bottom of the chamber as a loose white powder. The chemical reaction may be represented by the equation

$$2NO_2+2NH_3+H_2O+O=2NH_4NO_3.$$

Previous investigators had noticed the formation of white fumes when oxides of nitrogen were mixed with ammonia, but these were always supposed to be ammonium nitrite.

Some chemists went so far as to deny the possibility of the process. It was shown at a soirée of the Royal Society in 1918, and has been in operation on a small scale at Woolwich since then.

In commencing the work on the direct preparation of ammonium nitrate, it was thought desirable to make some investigations on the stability of ammonium nitrite in solution. The conclusions arrived at by previous investigators were generally confirmed, and the results extended to stronger solutions than those previously employed. The most important result of this work was to show that ammonium nitrite solutions, when even feebly alkaline, were remarkably stable, whereas the presence of a trace of acid made the solution very unstable. The bearing of this on the direct preparation of ammonium nitrate by passing converter gas into solutions of ammonia was therefore clear. During the first stage of the absorption, whilst the solution remained alkaline, but little decomposition of the ammonium nitrite (with consequent loss as free nitrogen) was to be anticipated; whereas in the second stage, when the solution became acid, there was considerable loss from this cause. Although this decomposition in acid solution is considerably retarded by lowering the temperature, the loss of nitrogen would still be serious. Experiments in detail confirmed these conclusions.

The results showed that the reactions in solution followed the same course as those with aqueous alkalis, such as soda and lime:

(i.) $2NH_4OH+2NO_2=NH_4NO_3+NH_4NO_2$.
(ii.) $2NO_2+H_2O=HNO_3+HNO_2$.
(iii.) $NH_4NO_2+HNO_3=NH_4NO_3+HNO_2$.
(iv.) $2HNO_2=H_2O+NO+NO_2$.
(v.) $2NO+O_2=2NO_2$.

In addition to these reactions in solution, however, a considerable amount of reaction appeared to take place in the gas. Dense white fumes were carried off from the solution when oxides of nitrogen were passed through aqueous ammonia. It was shown that, according to the conditions, the white fumes may contain up to 85 per cent. of ammonium nitrite, the rest being nitrate, or may consist of nearly pure ammonium nitrate. A method of condensing these fumes was discovered. So long as the fume remained moist it was found impossible to condense it, but as soon as it was dried by passage through concentrated sulphuric acid the fume at once separated spontaneously into the compact solid salt. It is not a little surprising that the ammonium nitrate is not retained by the sulphuric acid except to a very slight extent, and this method might be applied to the condensation of ammonium nitrate fumes in different technical operations—*e.g.*, the direct preparation of ammonium nitrate from gaseous ammonia and liquid nitric acid.

Having in this way overcome the difficulty of condensing the copious fumes produced, attention was next turned to the quantitative investigation of the reaction between converter gas and aqueous ammonia. If this white fume had not been collected, there would have been a loss amounting in some cases to 80 per cent.; the proportion of nitrate carried in the fume is therefore very considerable. The results of these quantitative experiments may be summarised as follows:

1. In all cases when ammonia *solution* is used there is considerable loss of ammonia as nitrogen (17 to 38 per cent.).

2. The nitrate produced always exceeds the nitrite, which would be expected owing to the loss of the latter by decomposition. At the same time some of the nitrite was probably converted into nitrate by the excess of oxides of nitrogen.

3. A considerable amount of ammonia is carried over unconverted.

4. Experiments with ammonium carbonate solution saturated with carbon dioxide (*i.e.*, NH_4HCO_3 solution) showed that no fume was produced nor ammonia carried away unchanged, but there was still a considerable loss of ammonia as nitrogen. The results of all these experiments showed that the interaction of *aqueous* ammonia and converter gas was not adapted to technical working.

The experiments described above led us to the conclusion that most of the reaction occurred in the gas, and experiments were therefore commenced with the object of examining the reaction between converter gas and gaseous ammonia. The results so far obtained may be summarised as follows:

By bringing together fully oxidised converter gas, the necessary amount of moisture, air, or oxygen, and gaseous ammonia, production of solid ammonium nitrate in a state of purity is attained. Under the present conditions of working there is still a loss in the form of nitrogen of from 10 to 20 per cent. of the ammonia, but it is possible that this loss may be further reduced.

In beginning and carrying out this research, we were not in possession of any information whatever as to what had been done, if anything, by other experimenters. The success of our process depends upon the careful attention to the proportion of the gases used, the amount of moisture, and the space available for reaction. Merely bringing together ammonia gas and converter gas usually leads to the loss of anything up to 90 per cent. of the ammonia as nitrogen.

It will be seen that this method in its present state of development is still attended with losses. It has the advantage of avoiding the use of water-absorption towers for nitric acid, and the subsequent neutralisation and evaporation of large bulks of liquid. Under the present methods of working the double decomposition of calcium nitrate with ammonium carbonate, as carried out by Messrs. Brunner, Mond and Company, the losses are not less than those involved in the new direct process, and the latter, besides avoiding the absorption towers, leads directly to the production of pure ammonium nitrate in the solid state. After an inspection of their plant we have no reason to believe that the considerable losses involved in the preparation of ammonium nitrate from calcium nitrate, as carried out by Messrs. Brunner, Mond and Company, were inherent in the process, or even at all necessary, and we therefore consider that the direct preparation of calcium nitrate from converter gas and lime, with subsequent working up to ammonium nitrate, is a process which deserves more consideration than has hitherto been accorded to it.

Ammonia Oxidation with Oxygen.

One of the main difficulties in the ammonia oxidation process is the absorption of the resulting oxides of nitrogen to produce nitric acid. This process, as usually carried out, requires an expensive tower system. Even if other arrangements than towers were adopted—and several have bee patented—the large space would still be required, since th reoxidation of the nitrous acid formed on contact of the gase with water must take place in the gaseous space, and a adequate amount of space must be allowed. Mr. Quinan, i is true, had an idea that some kind of intensive bubbler o scrubber, instead of towers, would solve the problem, an went so far as to take out a patent for such a scrubber of th well-known type. In his ignorance of the essential reaction involved, this inventor entirely overlooked the main difficult and attempted to provide for oxidation by separate space as had been done in other prior patents. Experiments showed as could easily have been predicted by anyone conversan with the problem, that the absorption did indeed take plac quite readily in the very small apparatus tried (a diameter o an inch or two was used), but that the product was mainl nitrous acid, which readily came out of solution again. It i not in this direction that the difficulty can be solved.

The loss in the tower system is due mainly to three causes:

1. The formation of a mist or fog of minute droplets o nitric acid when the gases containing oxides of nitrogen mixe with air come in contact with water in the first of the serie of towers. This mist is most difficult to condense; it passe almost without change through the remaining towers, an escapes as a mist from the exit. The engineers usually regar this mist as "traces of ammonium nitrate," and appear t be ignorant of the serious losses which may be caused in thi way. In our experiments this mist was condensed by electrostatic precipitation with aluminium electrodes, and found t be nitric acid of about 50 to 60 per cent. strength.

2. The increasing slowness of the reaction of absorption in the water or dilute acid as the content of oxides in the gas becomes smaller.

3. The increasing slowness of reoxidation of nitric oxide formed in the tower reactions, or present in the insufficiently oxidised gas, to higher oxides which dissolve in water, as the gases become more and more dilute.

It is obvious that all these difficulties can be avoided if one factor, which is the cause of them all—viz., the dilution of the oxides of nitrogen with inert gas—is removed. If it were possible to carry out the catalytic oxidation of ammonia, using pure oxygen instead of air, or at least if air appreciably enriched with oxygen is used, the difficulties would mainly disappear.

A mixture of ammonia gas and pure oxygen is, however, violently explosive. Previous work on explosions, particularly that of Professor H. B. Dixon, of the University of Manchester, suggested that it might be possible to damp down the explosive properties of the mixture by adding steam to it, at such a temperature that condensation could not occur. The mixture would then be passed over the catalyst, and after conversion the steam would condense without leaving any gaseous residue.

Experiments made by the authors in conjunction with Dr. G. N. White showed that this process is entirely satisfactory. The mixture of gases can be prepared by volatilising 25 per cent. ammonia solution at a controlled rate in a current of oxygen gas. The mixed gas is preheated in iron and aluminium tubes to about 500° C. and passed directly to the platinum converter. A very rapid conversion takes place with a production of 1·9 tons of nitric acid per square foot of double gauze catalyst per twenty-four hours, with an efficiency of practically 100 per cent. The nitric acid is readily condensed in coolers, without the use of any form of tower system. If oxygen could be obtained cheaply, say as a by-product in the manufacture of nitrogen in fixation industry, this method of oxidation is by far the best.

Ammonia Oxidation in British Industry.

It has already been stated that the application of ammonia oxidation to sulphuric acid chamber-processes has been adopted with success in this country. The apparatus is, with modifications, based on that devised by the writers in 1917.

As a result of the work referred to, the Minister of Munitions in 1917 appointed an Executive Committee, which held conferences with a number of manufacturers likely to be interested in ammonia oxidation on a larger scale. Among these firms were Messrs. Brunner, Mond and Company, the United Alkali Company, Messrs. Chance and Hunt, Messrs. Nobel and others. In August, 1917, this work in the laboratories of the Munitions Inventions Department, which had been commenced in October, 1916, with no information or apparatus available, had reached such a stage that the installation and trial of a full-scale unit, about four times the size of the laboratory units, was the only remaining step necessary for providing the data for the erection of a factory. This trial, which would require the erection of a more extensive tower system than could be accommodated in the Research Laboratory, was sanctioned by the Minister, and arrangements were made for a trial unit with an output of 300 tons of nitric acid per annum. A site in London and every facility were put at the disposal of the Ministry by a member of the Committee.

At this stage, however, the work of establishing the process on a commercial scale was abruptly taken over by the Department of Explosives Supply, as a result of a request made by that Department to the Executive Committee. The Department of Explosives Supply, apparently, had on its staff no one with sufficient knowledge of the problem to go forward with the work, since the trial unit was never set up. This is much to be regretted, as the results would undoubtedly have been of great value. In the course of further proceedings, as a result of a memorandum from the Department of Explosives Supply to the Munitions Council, it was decided that the cyanamide process could not be installed in less than eighteen months, and the erection of a factory for the production of synthetic ammonia was recommended, which, "granted good facilities, should be producing within a year." This, of course, was the Billingham factory, which is still not producing, in spite of the fact that the process has since 1919 been "undertaken [by Messrs. Brunner, Mond and Company] under such conditions and auspices as will secure its immediate and vigorous prosecution on a scale commensurate with its supreme importance." As a result, neither the fixation of nitrogen nor the oxidation of ammonia has materialised.

PART II

BY-PRODUCT AMMONIA AND AMMONIUM SULPHATE MANUFACTURE

ONE of the world's great sources of ammonia and ammonium sulphate is the combined nitrogen contained in coal, shale, and other organic matter. The amount of combined nitrogen in coal and shale varies from 0·5 to 2 per cent., and although only a portion of it is recovered as ammonia by means of the destructive distillation processes in commercial use, the scale on which the industries are carried on results in a large output of ammonia and ammoniacal compounds.

The main industries concerned in ammonia recovery in this country are those engaged in the manufacture of illuminating gas and of metallurgical coke, in the distillation of shale, in the production of power gas, and in the manufacture of pig iron with raw coal.

The economic position of many of these industries depends to an important extent upon the revenue obtained from the sale of ammonium sulphate, and with the ever-increasing demand for this salt for agricultural purposes, and the steady rise in its market price, the material has risen from the position of a by-product to that of a principal product in the industries concerned. This has resulted in the more extensive adoption of recovery plant in industries in which ammonia nitrogen was previously allowed to go to waste.

From a practical standpoint the ammoniacal liquors from gasworks, coke-oven plants, and shale works present many points of similarity. They all contain ammonia, carbon dioxide, and sulphuretted hydrogen, and differ principally in their strength; that produced in gasworks is usually richest in ammonia, while that obtained from coke-oven plants contains only about half the quantity in gasworks liquor. The weakest liquor is that produced from shale works (see Annual Report of the Chief Inspector under the Alkali, etc., Works Act for 1896).

Properties and Composition of Ammoniacal Liquor.

The destructive distillation of coal as carried out in gasworks practice produces a liquid having a colour varying from pale yellow to dark brown, and possessing a strong odour of ammonia, sulphuretted hydrogen, and of phenols ("carbolic acid").

It is obtained in three stages—

(1) By condensation in the hydraulic main, where the crude gas is cooled to 50° or 60° C.

(2) The condenser liquor, which may contain 2 to 3·5 per cent. of ammonia.

(3) The liquor obtained from the scrubbing and washing of the gas.

The strength of this liquor depends very largely upon the type of plant in use, but the liquor from all sources is usually collected, together with the tar, in a common storage well. The weak hydraulic main liquor may be used for scrubbing purposes, and becomes thereby itself more concentrated.

The conditions in coke-oven works are very similar to these, as far as the recovery of ammonia is concerned. The quantitative composition of the ammoniacal liquor will depend very largely on the nature of the coal which is carbonised, but the qualitative composition is not so variable.

Ammoniacal liquor is very complex in composition, the ammonia existing as various compounds. For practical purposes, however, these compounds are classed under two heads:

(*a*) Volatile (or "free")—*i.e.*, those compounds of ammonia which are volatile in steam.

(*b*) Fixed—*i.e.*, those compounds of ammonia that require the addition of an alkali such as lime to liberate the ammonia from them.

(*a*) *Volatile Compounds.*—The following are present: Free ammonia (the presence of which in the free state in ammoniacal liquor is doubtful), ammonium carbonate, ammonium sulphide, ammonium hydrosulphide, ammonium cyanide.

(*b*) *Fixed Compounds.*—Ammonium sulphate, ammonium sulphite, ammonium chloride, ammonium thiosulphate, ammonium thiocarbonate, ammonium sulphocyanide, ammonium ferrocyanide.

A comparison of ammoniacal liquors from various sources is given in the following table:

COMPARISON OF AMMONIACAL LIQUORS FROM VARIOUS SOURCES.

From	*Per Cent. Ammonia.*			*Per Cent. Sulphuretted Hydrogen.*	*Per Cent. Carbon Dioxide.*
	Free.	*Fixed.*	*Total.*		
Gasworks	1·572	0·229	1·801	0·234	1·857
Coke-oven plants ..	0·975	0·198	1·173	0·130	1·301
Shale works	0·573	0·036	0·509	0·026	0·938
Blast furnaces in iron works	0·257	0·035	0·292	Nil	0·526

(Averages taken from Annual Report for 1896 of the Chief Inspector under the Alkali, etc., Works Acts. For further particulars see this Report.)

Manufacture of Ammonium Sulphate from By-Product Ammonia.

The manufacture of sulphate at the largest gasworks involves the working up of large quantities of weak ammonia liquor by prolonged boiling in order to drive off and dissociate the volatile ammonium salts, the ammonia gas being absorbed in sulphuric acid. The liquor also contains a variable percentage of "fixed" ammonia, and this is set free by the addition of lime. Where the production of sulphate is aimed at, the apparatus is so contrived that the "volatile" ammonia is expelled by heat alone before the lime is added to decompose the fixed salts.

The absorption of the ammonia may be carried out in such a way as to yield a solution of ammonium sulphate, which is subsequently evaporated to produce a solid salt, or under such conditions that solid ammonium sulphate is produced directly, the heat evolved during the absorption in acid being sufficient to evaporate the water from the solution.

The average yield of ammonium sulphate at gasworks has been placed at 25 to 28 pounds per ton of coal carbonised.

The ammoniacal liquor was formerly neutralised directly with sulphuric or hydrochloric acid, the resulting solutions being evaporated for the recovery of the corresponding salts. The products, however, were by no means pure, and the ammonia is now recovered from the liquor as gas by distillation before being absorbed in sulphuric acid or otherwise utilised.

For the recovery of ammonia from this ammoniacal liquor the necessary distillation may be regarded as taking place in two stages.

In the first stage, the so-called *volatile ammonia*, representing the ammonia present as sulphide, carbonate, and cyanide, and in combination with the phenols, may be dissociated and volatilised by simply boiling the solution, say by blowing steam through it.

In the second stage, the *fixed ammonia* present as ammonium chloride, sulphate, thiosulphate, and thiocyanate, must be heated with a strong alkali in order that it may be recovered.

The fixed ammonia in average liquor may amount to 20 to 25 per cent. of the whole. The strength of the ammoniacal liquor is usually computed in "ounce strength"—*i.e.*, the weight of pure sulphuric acid, measured in ounces avoirdupois, required to neutralise the ammonia contained in 1 gallon of the liquor—and the volumes of liquor are usually converted into the equivalent volume of liquor of 10 ounces strength. The approximate strength of the liquor, however, may sometimes be deduced from its density, as it is found that each 1° Twaddell corresponds roughly to 2 ounces strength; but this is only used as a very rough-and-ready means of estimation.

Ammonium Sulphate, $(NH_4)_2SO_4$.

In the manufacture of ammonium sulphate the volatile ammonia is first driven off, the fixed ammonia being subsequently liberated by a further distillation with lime or soda.

The Grüneberg and Blum still consists essentially of three parts (Fig. 8).

There is first an economiser, *B*, where the liquor receives a preheating by means of the hot waste gases from the end of

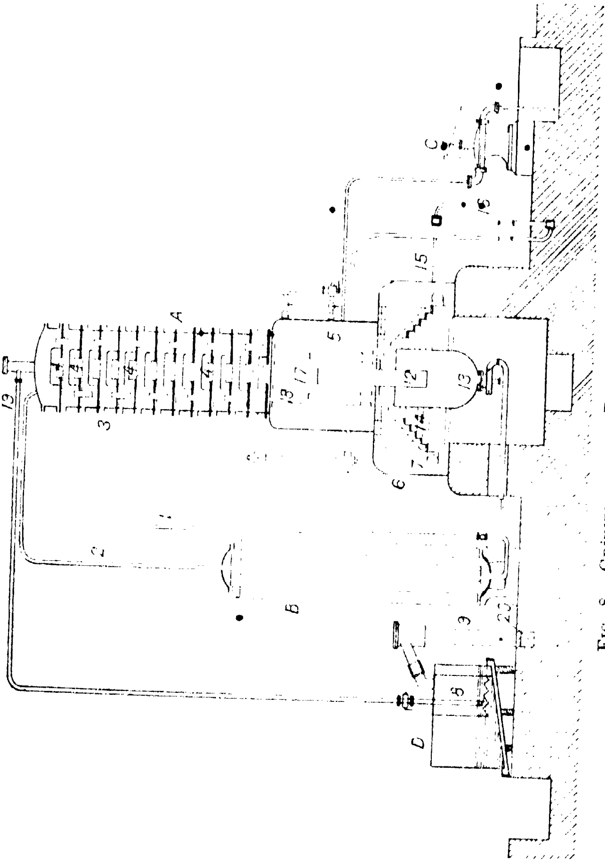


FIG. 8.—GRÜNEBERG AND BLUM AMMONIA STILL.

the process, or by boiler steam; secondly, a still, *A*, where the heated liquor is subjected to the influence of steam, whereby the volatile ammonia is given off, and where subsequent treatment with lime liberates the fixed portion of the ammonia;

thirdly, a saturator, *D*, where the ammonia gas comes into contact with sulphuric acid, ammonium sulphate being deposited.

The Supply of Ammoniacal Liquor.

Wherever possible, the ammoniacal liquor should be supplied to the superheater by gravitational means. For this purpose a cast-iron tank may be supported on girders at a suitable height, and it should be capable of holding several hours' supply. The tank should be covered by a wooden lid to prevent the escape of ammonia, a small vent being allowed to facilitate filling and to allow of even and uninterrupted delivery of liquor. A float and gauge should be arranged to give an indication of the supply to the plant, and in addition a small regulating tank should be inserted on the supply pipe before it joins the superheater, controlled by a float and ball-cock of cast iron. (Ammoniacal liquor speedily acts upon copper or brass.) This regulating tank should itself be a sufficient height above the superheater to allow of gravitational supply, which is regulated by a cast iron gland cock.

Superheaters.—In a sulphate of ammonia plant the purpose of the superheater is (1) To heat the ammoniacal liquor previous to its entering the still, by which means the consumption of fuel is reduced and also the capacity of the still to deal with the liquor increased. For this purpose the waste gases from the saturator are utilised. (2) To cool these waste gases to a temperature suitable for the further treatment mentioned below. It will thus be seen that a double object is achieved by the use of a superheater.

A form in extensive use is shown in Fig. 9. It will be seen that it is in principle an ordinary "battery" condenser erected vertically. The shell and the perforated horizontal plates are of cast iron, while the vertical tubes are fashioned in wrought iron. The joints between the ends of the tubes and the perforated plates are made by expanding the ends of the tubes in the usual manner.

The ammoniacal liquor enters the bottom chamber *a*, through the tube *b*, and rises through the wrought-iron tubes to the middle chamber *c*. It then passes through the second set of wrought-iron tubes to the top chamber *d*, whence it overflows along the pipe *e* to the top chamber of the still at

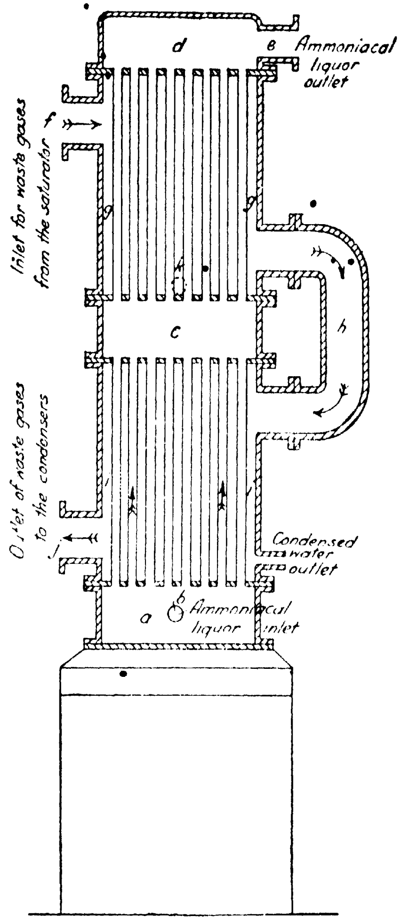

d
e
Ammoniacal liquor outlet
Inlet for waste gases from the saturator
f
g
c
h
Outlet of waste gases to the condensers
j
i
Condensed water outlet
a
b
Ammoniacal liquor inlet

FIG. 9.—SUPER-HEATER.

a temperature approaching 93° C. The waste gases from the saturator first pass through a baffle box in order to prevent any acid spray being mechanically carried forward and then enter the superheater by the pipe *f*. The baffle box for the waste gases usually takes the form of a short, wide tube lined with lead, and provided with a number of circular perforated lead discs against which the wet gases are caused to impinge. The moisture condensed in the baffle box is led back through a trapped tube to the saturator. On entering the superheater the gases pass over the outsides of the wrought-iron tubes in the chamber *g*, and then pass along the pipe *h* into the chamber *i*, where they again play upon the outsides of the wrought-iron tubes, and are finally conducted away along the pipe *j* to the condensing plant.

The condensate from chambers *g* and *i*, known as "devil water" from its disagreeable nature, is led away to a suitable seal pot to be subsequently dealt with.

Stills.—In the apparatus of Grüneberg and Blum (Fig. 10) the first portion of the still, 3, in which the volatile ammonia is liberated, consists of a number of compartments, separated by horizontal division plates, through which the liquor flows downwards by means of overflow pipes, steam travelling upwards in the reverse direction. By suitable arrangement the steam is caused to bubble through the liquor in each compartment, whereby the volatile ammonia and also the volatile acids present—namely, carbon dioxide, sulphuretted hydrogen, and hydrocyanic acid—are evolved.

The second portion of the still consists of a lime vessel, 5, into which milk of lime is pumped at intervals of ten minutes, and also possesses a boiler with an internal cone, 14, in which the liquor is boiled in thin sheets by means of steam. The last portions of ammonia are here set free. The mixed steam and ammonia vapours leave at the top of the dephlegmating column by the pipe 19, and enter the saturator *D*, which is charged with sulphuric acid, the exit gases from which serve to heat the liquor in the economiser.

The earlier "single-column" type of still was very apt to give trouble owing to the frequency with which it became choked. This difficulty was not so apparent in that portion in which the votalile or "free" ammonia was set free as in the liming chamber and the compartments immediately below it. The construction of the still was such that it was necessary to dismantle the volatile ammonia section in order to reach the obstructed portion, and the first important development in plant design was to erect the "volatile" and "fixed" sections upon separate bases. The liming chamber was placed either at the bottom of the former portion, in which case accessible manholes were provided to facilitate cleaning, or at the top of the latter portion. Such an arrangement is used in the Feldman still and in Colson's plant, and when room permits similar arrangements may be obtained in the various other types of still. Brief consideration may be given to a British type of still (Wilton's), which, while it retains all the advantages of the earlier types, also provides efficient methods for effective cleaning without the necessity for dismantling.

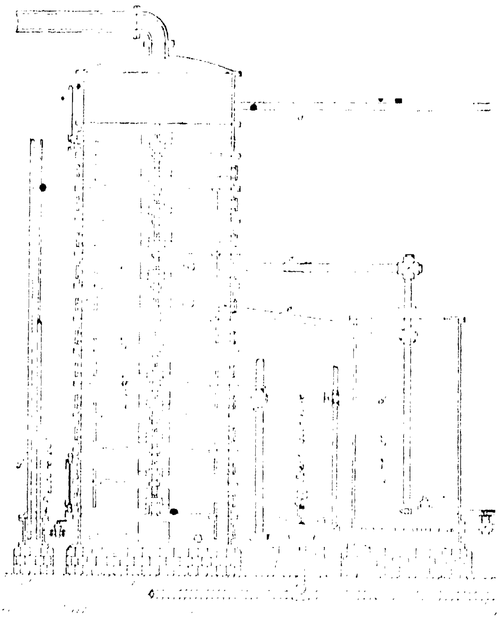


FIG. 10.—WILTON AMMONIA STILL.

Wilton Still (Fig. 10).—The ammoniacal liquor enters the still from the superheater along the pipe *a*, and passes from chamber to chamber in the usual way until the one marked *b* is reached, when, instead of passing through the overflow on the right below *f*, the liquor descends through the pipe *c*, by gravitation, to the liming still *d*, and passes back to the liquor still, mixed with milk of lime, along the pipe *e*, and then descends in the usual course through the remainder of the still, leaving by the waste liquor valve, described later. The position of pipe *c* is rather lower than shown in the diagram, in order to compel the liquor to take that course in preference to rising and overflowing over the overflow pipe below *f*. At *g* is shown an efficient form of safety valve for an ammoniacal liquor still.

Liming Apparatus.—This portion of the plant is concerned with the dissolving of the lime and its introduction into the still. The lime may be slaked either by waste liquor from the still or by hot or cold water. The use of waste liquor possesses the advantage that should the contents of the still at any time become deficient in lime, a strong smell of ammonia becomes evident when the spent liquor comes in contact with the lime in the dissolving tank. This serves as an efficient warning to those in charge of the process as to the conditions prevailing in the still, and enables them to take steps promptly to rectify matters.

The best points at which to tap off the supply of waste liquor are (1) the bottom chamber of the still; (2) the pipe leading from this chamber to the seal pot; or (3) from the seal pot itself, but it must be ensured that there is sufficient pressure or head to supply the liming plant. The use of a hot liquid for slaking results is a considerable saving of fuel compared with the use of cold water, and in cases where the former is adopted it is desirable to allow the steam given off to escape by means of hoods and wooden chimneys of standard pattern.

In a typical liming apparatus the slaking of the lime is carried out in a tank, the milk of lime being tapped through a screen into a second tank, whence it is pumped by a single ram pump into the liming chamber of the still. An agitating arrangement is also worked by the pump, and this prevents settling of the lime.

A regular strength of the milk of lime and consequent steady working is thus obtained. The screen is covered with wire gauze of about ¼ inch to $\frac{3}{16}$ inch mesh, and care must be taken to maintain this gauze in good condition, as the presence of any holes allows small pieces of lime to pass through. These are very liable to give much trouble in the valves of the pump, resulting in the still running short of lime and causing "high" spent liquor samples.

Where a driving shaft is available, the lime-mixing arrangement shown in Fig. 11, is found to be very efficient. The waste liquor is run into the circular tank *a*, and the lime is fed gradually on to the perforated plates *b*, the rate of solution being accelerated by means of the mechanical stirring contrivance *c*. The undissolved material is removed from time to time, and if its relative weight compared with the weight of lime used be ascertained it forms a good guide as to the quality of the lime.

The milk of lime runs by way of the cock *d*, through the screen *g*, into the tank *e*, whence it is pumped through the suction pipe *f* to the liming chamber of the still. In the tank *e* the contents are kept agitated by a similar arrangement to that in the tank *a*.

The waste liquor outlet pipe from the bottom of the still is usually provided with a cock to regulate the flow of liquid. The escape of any live steam is prevented by means of a suitable seal pot also inserted in the pipe run. An example of such a seal pot is shown in Fig. 12, this being a suitable form for sinking in the ground when desirable. If the seal pot is mounted in any enclosed space where the escape of steam is objectionable, a cover may be provided, with a vent pipe to lead the steam away, but where the escape of steam is not objectionable an open pot possesses the advantage of assisting in the cooling of the spent liquor.

The seal pot is sometimes replaced by a boiler through which the spent liquor is led, the boiler being utilised as a means of raising the temperature of either water or ammoniacal liquor passing through a coil of pipes, the requisite seal being obtained by regulating the height of the waste liquor outlet pipe. This method, however, cannot be recommended, as the lime sludge quickly deposits upon the pipes and renders them ineffective, and the necessary cleaning is then a matter of considerable difficulty.

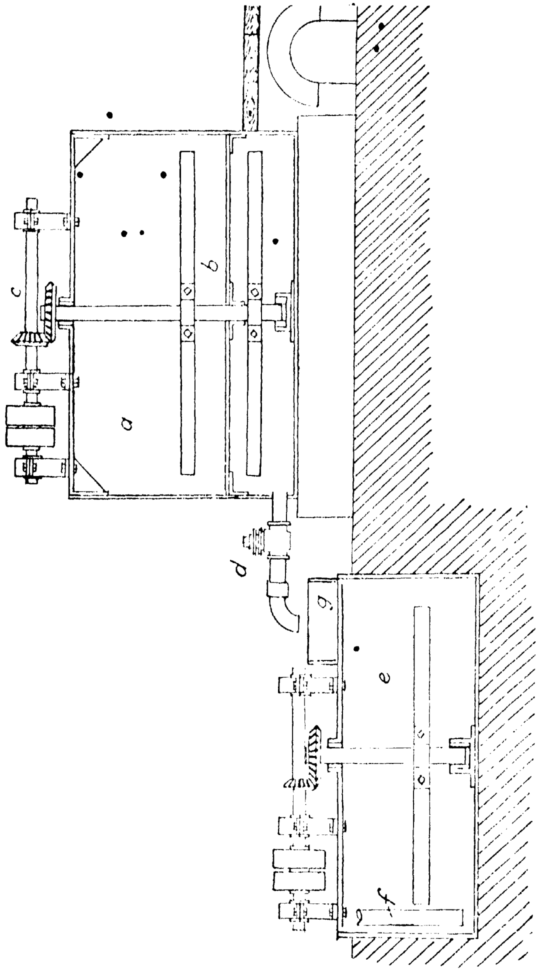


FIG. 11.—LIME MIXER.

From the seal pot or automatic valve the spent liquor is conveyed by flanged pipes, or open troughs of cast iron, wood, or bricks laid in cement, to the settling and cooling tank. Where the escape of steam is not objectionable, the open trough is preferable, as it not only assists in the cooling, but is also easily cleaned. Where pipes are used they will require to be taken up frequently for cleaning purposes, so that the advantage of flanged over socket pipes for this purpose is obvious.

FIG. 12.—SEAL POT.

Saturators.—The saturator may be constructed either of solid lead throughout, or of wood or iron lined with lead. Referring once more to Fig. 8, the gases are led in by means of a perforated leaden pipe, fixed in a leaden bell, 8, which distributes them over a considerable area in the saturator. The unabsorbed gases pass through 9 into 20, where any liquid carried over is retained.

Sulphuric acid of about 140° Twaddell strength (77 per cent. H_2SO_4) is generally used, which soon becomes nearly saturated (indicated by its colour), crystals of ammonium sulphate being deposited. These are removed from time to time, fresh acid being introduced to replace that neutralised.

When working properly, the steam and water gauges will remain steady, and the reaction in the saturator will proceed gently.

Carbon dioxide must be eliminated before the liquor reaches the lime vessel, as otherwise the apparatus is liable to become obstructed with calcium carbonate. The waste liquor, which issues at 16, should not contain more than 5 parts NH_3 in 100,000.

Saturators may be divided into three main types, depending upon the method by which the sulphate is removed:

(*a*) Those from which the sulphate of ammonia is removed by "hand fishing." This type is open to the air.

(*b*) Those from which it is removed by means of a steam ejector, and which may be either covered in or open.

(*c*) Those from which it is removed by means of a suitable bottom discharge valve. These are generally totally enclosed.

(*a*) *Open Hand-Discharge Type.*—A simple type of open saturator suitable for hand fishing is shown in Fig. 13. This consists essentially of a wooden tank formed of 9-inch by 3-inch redwood, securely bolted together and lined with sheet lead of 20 pounds per square foot. Best soft chemical lead should be used throughout the plant. The mid-feather *a* is of cast lead about ½ inch thick, stiffened by a border and ribs, an extra 1 inch thick. The ammoniacal gas enters the saturator through the pipe marked *d*. From the flange joint *e* this is made of drawn lead pipe from 4 inches to 6 inches in diameter, according to the size of the saturator. The end nearest the fishing pocket *f* is bossed up, and a lead flange of suitable size is cast and "burned" on the top end. A number of ¾-inch holes are drilled in the pipe in either one or two rows, each hole being drilled at an angle so that the ammonia blows towards the fishing pocket. An iron pipe conducts the ammonia from the still to the saturator, and just before its connection to the pipe *d* a ½-inch hole is drilled which is closed by the tapering wooden plug marked *g*. During the cooling of the still, when operations have been stopped, this is removed in order to prevent the contents of the saturator being sucked back.

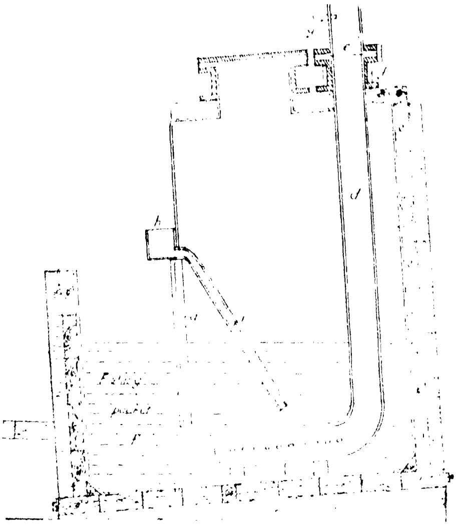


Fig. 13.—Hand-Discharge Saturator.

The acid and mother liquor are supplied to the saturator from two overhead tanks along lead pipes discharging into the small tank *h*, the flow being controlled either by regulus taps or earthenware taps covered with lead. The supply to these pipes may be conveniently cut off at the tank end, either by means of regulus plugs and seats or by a siphon box. Either of these methods is suitable for the supply of sulphuric acid, but the mother liquor supply should be fitted with the siphon box, as it often becomes necessary to remove adhering crystals by means of hot water. Around the plug is placed a large pipe made from sheet lead, the bottom portion of which is perforated with holes. This prevents clogging of the pipe and taps with foreign matter. The provision of one of these arrangements enables any repairs to be done to the tap without emptying the tank. The pipe *i* (Fig. 13) should be of sufficient length to ensure its remaining sealed under all circumstances, in order that there may be no escape of noxious gases.

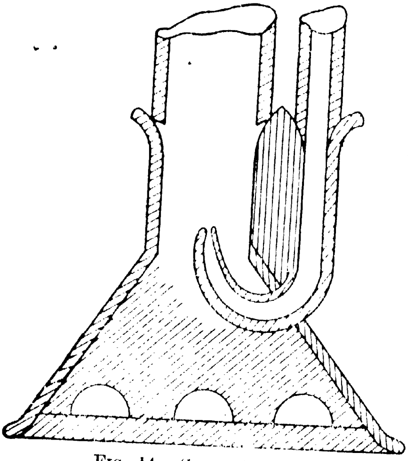


FIG. 14.—STEAM EJECTOR.

As the sulphate of ammonia is formed it collects in the fishing pockets, whence it is removed by means of copper scoops or shovels, fitted with long pitch-pine handles.

(*b*) *Steam Ejector Discharge Type.*—In this type of saturator the sulphate of ammonia is removed from the saturator by means of a steam ejector, as shown in Fig. 14.

The open form of this saturator is essentially the same as those already described. In this case, however, the flat-bottomed pocket for hand fishing is replaced by a well such as is shown in Fig. 15, in which the sulphate of ammonia collects in a manner convenient for ejection.

The closed type of steam ejection saturator is the most modern, and the advantages it possesses in freedom from smell and in labour-saving conveniences as compared with the older hand-fishing type give it popularity in spite of its apparent complication.

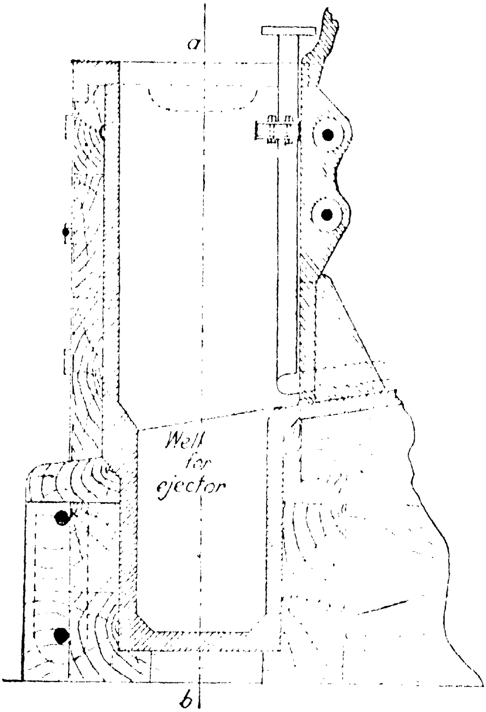


FIG. 15.—WELL FOR STEAM EJECTOR.

A circular form of the apparatus, made of plate lead and fitted with a steam ejector as supplied by Messrs. Joseph Taylor and Company, is shown in Fig. 16. A seal pipe is inserted as shown to enable samples for testing to be withdrawn, and in order that the depth of mother liquor present may be observed. The sulphate of ammonia is discharged

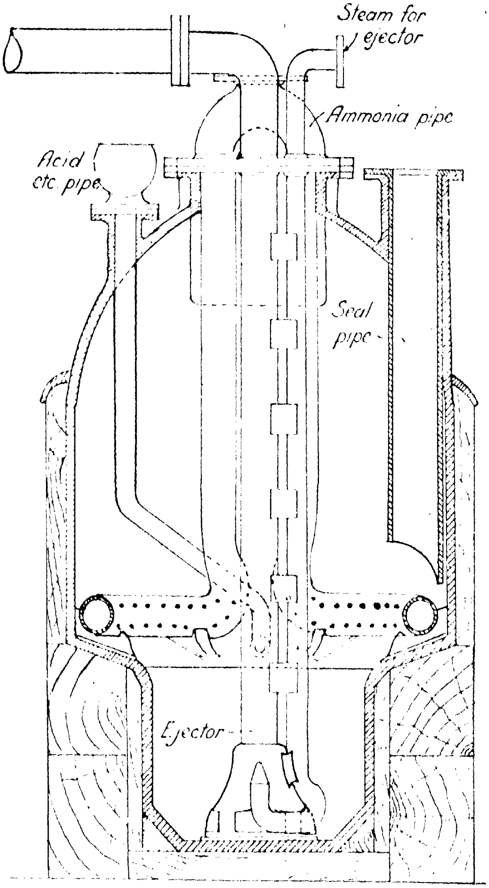


FIG. 16.—SATURATOR WITH STEAM EJECTOR.

from the ejector straight on to draining tables, or into corves standing over a draining floor.

(c) *Bottom Discharge Valve Type of Saturator.*—This type provides a most satisfactory arrangement, and Colson's form of the apparatus consists of a body of cast-iron sections lined with lead, the whole being strongly bolted together.

Draining.—The crystalline ammonium sulphate is periodically removed from the saturator and placed upon draining tables. These draining tables are constructed of 9-inch by 3-inch planks on edge, except across the end of the fishing pocket. They are provided with a lead lining (10 pounds per foot), this lining being turned over across the end of the fishing pocket to form a gutter in order to allow the mother liquor to flow back into the saturator in a clean manner. Upon the leadwork are laid pieces of pitch-pine, 3 inches by 3 inches, at intervals of about 1 foot. These support pitch-pine boards, 6 inches by 1 inch, upon which the salt is placed as it is scooped out of the well of the saturator. The drainage of the salt is thus facilitated, and the leadwork protected. From the draining tables the salt is periodically transferred to the floor of the store, where, after being allowed further time for drainage, it is stacked in heaps for packing.

The time that the salt will require to lie in store before packing will necessarily vary somewhat, but under normal conditions about three to four days should suffice.

The tanks for the mother liquor should be of sufficient size to allow of ample storage room during the starting up of the plant, or during temporary stoppage. The total storage for mother liquor should be at least three times the capacity of the saturator.

The mother liquor obtained from the draining of the salt is collected into tanks, and is subsequently pumped by means of an acid elevator, or regulus metal steam injector, into the tank supplying the saturator.

Hydro-Extractors.—In order to shorten as much as possible the drying time of the salt after manufacture, hydro-extractors or centrifugals are sometimes made use of. These consist essentially of an outer cast-iron circular vessel inside which is fitted a copper container, the sides of the latter being perforated with a large number of small holes. This inner vessel is filled to a convenient height with the sulphate of ammonia as delivered from the draining tables or corves. The copper vessel is then caused to rotate at a very high speed, this resulting in the salt being forced against the sides, the moisture being expelled through the holes in the vessel into the outer casing, through the outlet of which it finds its way on to the draining floor beneath. The time required to effect this drying will vary according to the condition of the salt as put into the "hydro," but will usually range from two and a half to four minutes, according to the state of dryness required in the final product.

Care must be exercised in fixing the conditions under which the salt is finally bagged. Immediate packing after hydro-extraction may result in the sulphate setting very hard, with detriment to the fabric of the bags.* The heap obtained from the hydro-extractor should be turned over a few times, and allowed to stand a few hours, before packing.

The product as usually marketed is a salt of light grey colour, which is guaranteed to contain a minimum of 24 per cent. ammonia (NH_3). It usually contains from 24·25 per cent. to 24·75 per cent. NH_3, from 2 to 4 per cent. of moisture, and is usually slightly acid, to the extent of 0·15 to 0·4 per cent. uncombined sulphuric acid (H_2SO_4). The greater part of the sulphate of ammonia produced is used as a manure either by itself or combined with other substances, and for this reason freedom from cyanides, which are deleterious to plants, is often a specified property on the part of the buyers.

On prolonged storage under certain conditions, or by longer hydro-extraction, the sulphate may lose so much moisture that the NH_3 content may rise as high as 25·25 per cent. Such a salt, especially if also of fairly white colour, usually fetches the top market price, but the little extra price secured scarcely pays for the extra ammonia above the 24 per cent. guaranteed in the normal way.

Waste Gases.—That portion of the gases from the still which remains unabsorbed by the sulphuric acid in the saturator consists very largely of carbon dioxide, sulphuretted hydrogen, and moisture, together with traces of pyridine, cyanogen compounds, and many other substances. These waste gases, which have an intensely objectionable odour, after leaving the saturator pass through a baffle box to the superheater, as described above, where by heat exchange the temperature of the ammoniacal liquor is raised to about 93° C. The exit gases from the superheater have to be still further cooled to fit them for subsequent treatment. A simple form of apparatus for accomplishing this purpose consists of a series of thin cast-iron pipes, over which is placed a 2-inch or 3-inch wrought-iron water pipe pierced on its under-surface with small holes. This is connected with a suitable water-supply, and by means of a cock the supply is adjusted to secure the cooling of the gases to the temperature of the air.

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* On the "setting" of salts, see T. M. Lowry and F. C. Hemmings, *J. S. C. I.*, 1920, 101 *T*.

After the waste gases are cooled and dried they may be dealt with in one of three ways viz.:

(1) Converted into sulphuric acid by burning in connection with a chamber plant.
(2) Converted into sulphur by the Claus process.
(3) Passed through an oxide of iron purifier, such as is used in gasworks.

The *iron oxide purifiers* consist of boxes containing trays covered with hydrated oxide of iron ($Fe_2O_3,3H_2O$), over which gas (*e.g.*, coal gas) containing sulphuretted hydrogen (H_2S) as impurity passes. The sulphur is retained in the form of iron sulphide: $Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$. When the oxide is converted into sulphide ("spent oxide") it is "revivified" by exposure to air: $Fe_2S_3 + 3O = Fe_2O_3 + 3S$. When, after alternate use and revivification, the mass contains about 50 per cent. of free sulphur, it is burned in air to supply sulphur dioxide to acid plants.

The Preparation of Ammonium Sulphate by the Direct Process.

An interesting plant was erected by Mr. George Wilton in 1910 at a small gasworks carbonising about 2,000 to 2,500 tons of coal per year (see Forty-seventh Annual Report of the Chief Inspector of Alkali Works, 1910, p. 66). The object of the new plant was to deal satisfactorily with the ammoniacal liquor, and particularly the effluent from the sulphate of ammonia manufacture, which contains sulphocyanides and phenols. Although this plant was installed in a small works, the process appeared suitable also for works of much larger size. The hot coal gas from the hydraulic main was passed through a condenser or specially constructed washer. In this apparatus the gas entered at the bottom, in such a manner that the condensed liquor ran away warm, and in consequence contained very little free ammonia. The upper part of this condenser was used as a naphthalene arrester, containing a suitable solvent for this material. The last traces of tar in the gas were also arrested by this means. Suitable arrangements were also made in order that, if necessary, the gases leaving the condenser could be cooled. The gases then passed through the exhauster and entered a lead-lined sulphuric acid washer. Fresh sulphuric acid was added from time to time to this absorber in such a manner as to keep the solution to a content of 1 per cent. of free acid. When the solution in the washer had reached a certain strength some was withdrawn and forwarded to an evaporator, which consisted of a lead-lined pan fitted with a steam coil; the solid crystalline sulphate of ammonia was thus produced. The whole of the ammonia in the gas was said to be absorbed in the washer, and by the employment of weak sulphuric acid the illuminating power of the gas was said to remain unaffected. The virgin liquor containing ammonia in the "fixed" condition was pumped into a tank, and from there flowed into a direct-fired still. This still consisted of a small column, from which the liquor, after admixture with milk of lime, flowed into three circular tubes, horizontally placed in the furnace. The ammonia and steam given off in these evaporators were admitted to the column, and effected the necessary distillation of any free ammonia in the liquor there. From the column the liquor passed into the acid washer for the coal gas previously described. There was no preliminary water scrubber in the gas plant, the virgin liquor resulting from the moisture in the coal, and the acid liquor employed in the washer being the only water introduced into the process. It was stated that the effluent was in this way reduced to one-fourth as compared with the ordinary sulphate of ammonia plant, and the process had this fact to recommend it in cases where effluent disposal was a matter of some difficulty. At the start the process was adopted only in works of small size, but it became in more extended use and was in successful operation in works making 500,000 cubic feet of coal gas per day. In 1915 twenty-one plants were under inspection. The operation of the process seemed to cause a certain amount of trouble in the oxide purifiers. Moreover, the yield of sulphate of ammonia was at times very variable. The latter in the majority of works was, in 1915, much below the anticipated figure; out of thirteen works from which returns were received five works had recovered less than 17 pounds of sulphate of ammonia per ton of coal carbonised, six less than 18 pounds, ten less than 21 pounds, eleven less than 25 pounds, and at two works only had the make exceeded this figure with a yield approaching 28 pounds. The figures were disappointing, in that, properly worked, the process should undoubtedly have yielded a return exceeding that obtained with the older process, which averages 22 pounds of sulphate of ammonia per ton of coal carbonised. Storage losses of ammonia would, in general, be greater with the older process, which necessitates the handling of large volumes of ammoniacal liquor relatively rich in "free" ammonia. An enquiry was undertaken in the hope that by a close study of the conditions at various works and by careful analysis of the products data might be obtained which would indicate the directions in which improvement might be looked for, both with respect to more regular working of the purifiers, and a higher yield of sulphate. The following conclusions were arrived at with regard to the conditions under which the purifiers might be expected to maintain good efficiency:

1. The "moisture" content of the oxide in the purifiers should be from 5 to 10 per cent., such hydration having regard rather to the reactive ferric hydroxide content of the mass than to the total mass of material, active and inert.

2. **Temperature.**—(*a*) The crude gases entering the system should be dry and cool rather than moist and warm. It is essential that the moisture content should be low.

(*b*) *Oxide.*—The temperature of the mass of oxide should approximate to 21° C. in order that the gas may carry away as vapour the whole of the moisture equivalent to the sulphuretted hydrogen absorbed. The conditions should be adjusted so that the water of hydration set free and retained in the sulphide mass may be reabsorbed through hydration of re-formed ferric oxide, and not carried away in the exit gas.

3. **Impurities.**—The crude gas should be freed as far as possible from tar fog, oils, naphthalene, and hydrocyanic acid, but should contain 0·5 to 1 grain per 100 cubic feet of ammonia, and also oxygen equivalent to half the volume of sulphuretted hydrogen present.

4. **Purifier Boxes.**—These should be protected from the cold, and should be worked in rotation in such a way as to bring the material richest in ferric hydroxide into contact with gas richest in sulphuretted hydrogen, and the material richest in sulphide into contact with gas poorest in sulphuretted hydrogen.

5. **Direction of Flow.**—It is best that this should be downwards.

6. **Regulation of Working**—The conditions throughout should be as regular as possible.

(See Fifty-second Annual Report of the Chief Inspector of Alkali Works, 1915, p. 27.)

The following is an account of the detailed working of the direct ammonium sulphate plant at one of the works under inspection:

Virgin Liquor Still.—Test of the effluent liquor showed that on occasions serious loss of "free" and "fixed" ammonia was taking place; the still was overtaxed, and milk of lime added with little regard to the volume of liquor charged, thus:

(i.) *Virgin Liquor Feed.*—"Free" ammonia, 1·040; "fixed," 0·880; total, 1·920.

Effluent Spent Liquor.—"Free" ammonia, 0·066; "fixed," 0·330; total, 0·396—a loss of 20 per cent., equivalent to 3 pounds sulphate of ammonia per ton of coal carbonised.

(ii.) With increased lime feed and more careful steaming, *effluent spent liquor* showed "free" ammonia, 0·046; "fixed" ammonia, 0·003; total, 0·049—a loss of 2½ per cent., equivalent to ⅓ pound of sulphate of ammonia per ton of coal.

It was then decided to charge the still periodically with the same volume of liquor and to add a fixed charge of milk of lime, to work the top section of the still hot, and to increase the flow of water into the condenser. The altered procedure was entirely successful; in place of 17 to 20 gallons of liquor for seventy minutes, 25 gallons were distilled, and loss of ammonia in the spent liquor was minimised. But the improvement was only made possible by consequent changes in the absorber; to cope with the extra volume of ammonia from the still it was necessary to secure partial or complete separation of the ammoniacal condensate from the Liebig condenser, otherwise the effluent bubbler liquor was found alkaline under all conditions of work. This was effected by means of a small preliminary "neutralising box" placed in the acid liquor circuit; the ammoniacal condensate and uncondensed gases were passed through this box with the acid liquor before entering the bubbler. Complete neutralisation was thus effected in a simpler manner and at minimum cost, as all the parts were made and fixed by local labour. The arrangements are shown diagrammatically in Fig. 19.

In Fig. 17, *A* is the neutralising box, a lead-lined wooden box 3 feet square by 18 inches high; *B* is the usual iron seal pot receiving ammonia gas and condensed liquor from the Liebig condenser, *C*; *D* is the usual lead box for circulating liquor from the bottom of the bubbler *E*, raised 2 feet and connected with *A* by 1-inch pipe sealed in liquor below from the neutralising box *A*; The mixed ammoniacal and acid liquors enter the bubbler by the usual pipe *a*, sealed below, and uncondensed gas by the usual unsealed pipe *b*. Feed pipe *F* delivers strong sulphuric acid direct from overhead tank to the last compartment of the effluent liquor tank, in place of the lead box as formerly.

The following is a description of the plant operated at a works carbonising an average of some 40 tons of coal per twenty-four hours, with an average of about 13,000 cubic feet of gas per ton of coal carbonised. This works possesses four oxide purifiers, each 24 feet square and containing three layers of oxide 9 inches deep. The purifiers are built on columns, and are exposed to free circulation of air, but under a roof.

They are worked in sequence with upward flow of gas, and the first box is emptied when a foul test is obtained at the exit of the third. Revivification of the spent oxide is carried out on the floor of a large shed.

The *acid bubbler* is 6 feet square by 4 feet high, with the usual effluent tank and lead box for circulation of liquor.

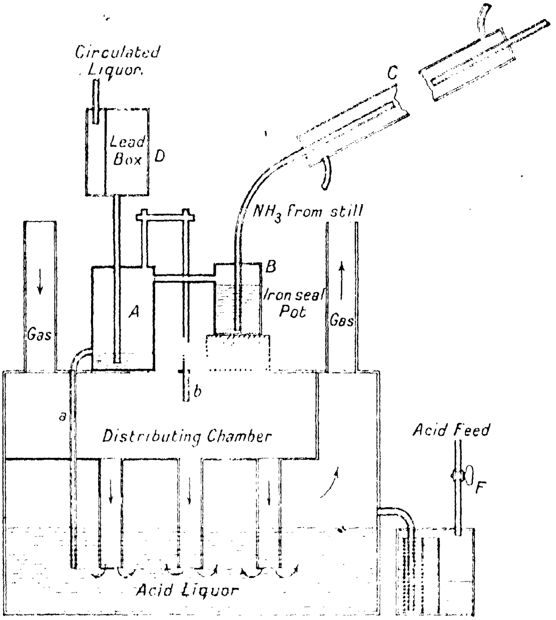

FIG. 17.—NEUTRALISING BOX.

Before entering the absorber the crude gas passes through a washer fed with ferrous sulphate for removal of hydrocyanic acid. The bubbler also receives ammonia from a continuous still fed with virgin liquor, and on occasion from a small still attached to the cyanide recovery plant. After passing through the bubbler the crude gas traverses a long underground main (100 yards) before entering the purifiers.

The *virgin liquor still* is continuous, with automatic lime feed. The vapours are partially cooled by a Liebig condenser, the condensed liquid flowing to an iron seal pot placed above the bubbler. The exit from the seal pot has been altered to deliver the ammoniacal liquor and uncondensed gases to the inlet gas mains in place of the bubbler direct, to minimise the risk of local alkalinity.

The *cyanide recovery still* is a small vertical still for removal of free ammonia from the cyanide sludge; the distillate enters the iron seal pot named above. Formerly "climbing" was a source of trouble, and a highly discoloured sulphate was obtained. To remove this difficulty, the gases from the still were led through a short length of iron pipe, 3 feet 3 inches in length by 10 inches diameter, placed close to the still, and with a draining pipe sealed in the third tray to remove condensed liquor. The salt is now of excellent quality (see Fifty-third Annual Report of Inspector of Alkali Works, 1916).

The working of plant for the manufacture of sulphate of ammonia in gasworks by what is known as the "Direct Process" was made the subject of special study and research during each of the four years 1915 to 1918, and the Alkali Reports for those years contain a detailed account of the investigations conducted at typical works, and the conclusions based on the data relating thereto.

The conclusion of the work in 1916 still found one faced with the fact that the yield of sulphate in the direct process remained low, when judged by relative standards, even at works where every effort was made to reduce working losses at the purifiers, storage tanks, and ammonia still to a minimum.

Further experience confirmed the conclusion previously reached that a regulated supply of ammonia is essential to efficient purifier working in the direct process, especially during the colder months, when the oxide boxes are working at full load, and one is disposed to attribute much of the irregularity of working during the colder weather to the free absorption of ammonia by a relatively wet oxide and its conversion into fixed salts—thiocyanate and sulphate. When oxide fouls during such periods of disorganisation it is usually found to possess an acid reaction and to contain marked traces of soluble ferrous salts, and that the free use of the ammonia by-pass has often enabled the foul box to clear itself if a suitable temperature be maintained.

In a paper read before the Southern District Association of Gas Engineers and Managers, on November 10, 1910, Mr. Phillip G. G. Moon summarised the financial advantages of working the Wareham plant as follows:

> "As there is no fuel or labour bill to be met, practically the only charges against the sulphate sold are the cost of the acid used and the interest and depreciation of the plant itself. The capital outlay is, however, so small, and the wear and tear of plant so inappreciable, that these charges do not amount to very much per ton. I estimate that, selling the sulphate of ammonia produced at £11 per ton, there will be a net profit of £7 per ton sold."

At works of the smallest size, such as Wareham, with an output, say, of 5 tons of sulphate per year, no attention was then paid to the collection and distillation of the virgin liquor that condenses. It was simply run to waste. The estimated loss of ammonia, though small in itself, perhaps, was relatively large, and was estimated at Wareham to amount to 5·1 pounds of ammonia per ton of coal carbonised. Undoubtedly the problem was thus greatly simplified for works where effluent liquors of this character could be discharged without complaint, both with respect to labour charges and purification practice. At larger works, such as Dunstable, where 2,000 to 3,000 tons of coal are carbonised yearly, with a production, say, of 25 tons of sulphate per annum, other considerations arise, and more elaborate and costly plant, with attendant increased charges for labour, had to be installed. To the acid washer was therefore added the ammonia boiler, which demanded the more or less constant attention of a skilled attendant.

The expectation formed at this early date of the volume of liquor to be distilled and of the effect of the admission of the ammoniacal vapours and accompanying gases to the acid washer have not been realised in subsequent experience. The boiler first introduced to deal with the virgin liquor soon gave place to an ammonia still of more modern type, and lately stills of the intermittent type at more than one works have had to be replaced by more powerful plant of the continuous type. The volume of virgin liquor calling for treatment at many works, far from being 10 to 12 gallons per ton of coal, often exceeds 18 to 20 gallons and even 30 gallons in exceptional cases. With the larger volume of liquor is condensed a larger proportion of ammonia in the crude coal gas leaving the retorts, and the virgin liqour often contains a larger amount of ammonia than that entering the acid washer direct with the crude gas. This is more especially the case during the "winter" months, when the volume of liquor will be at a maximum, due in part to the higher moisture content of the coal stored in the open, and in part to the increased condensing effect of air condensers and connections at winter temperature.

With the introduction of stills and the admission of the disengaged ammoniacal vapours direct to the acid washer there ensued, at several of the larger works, prolonged and disastrous periods of disorganisation at the purifiers, due to the overheating of the washers and the passage of an undue amount of moisture to the oxide boxes—disorganisation which at that period was only in part avoided by by-passing a large proportion of the ammonia direct to the purifiers.

The conditions for efficiency are now better known: the acid washer is kept cooler; drier oxide is now charged in the purifiers; boxes, where exposed, have been protected from the weather and their temperature regulated by thermometric data systematically recorded; and, of late, further improvement has been effected at the best-conducted works by the adoption of the "backward system" of oxide purification with downward flow of gases, in place of the older system of working the purifiers successively to exhaustion in series, and with upward flow of gases through the boxes in sequence. Further relief has been afforded, in certain cases, by the introduction of a "neutralising box" or "neutralising pipe" at the acid washer, to secure a better circulation of acid liquor within the system, and by the use of a preheater at the still; and, lately, at two of the works hoods have been erected over the evaporating pan and the vapours of steam and pyridine drawn away for discharge at a suitable level outside the sulphate house.

Technically speaking, the efficiency of the plant, as now operated in the best-conducted works, apart from the recovery figure for sulphate, leaves little to be desired; but the process still throws on the coal gas purifiers the burden of dealing with the whole of the foul gases in the crude coal gas leaving the retorts—carbon dioxide, sulphuretted hydrogen, and hydrocyanic acid—unlike the older distillation process, in which some 25 per cent. of the carbon dioxide, 7 per cent. of the sulphuretted hydrogen, and a notable proportion of the cyanogen compounds, are removed by washers before the crude gases enter the purifiers.*

The technical improvements noted above, though undoubtedly affording relief from the disorganisation at the purifiers, and effecting some conservation of ammonia formerly lost in the effluent still liquors and at the boxes, have done little to reduce the cost of labour in the sulphate house, and it is now a serious consideration with some managers whether economy would not be effected by a conversion of the acid washer or evaporating pan into a saturator of ordinary type, with storage of liquor for periodical operation of the still and with diversion of the foul gases to appropriate purifiers or oxide heaps. At three of the works, indeed, the "direct" process has now been replaced by one of the older distillation type, with marked improvement in the recovery figure for sulphate. At a fourth works replacement has been temporarily suspended pending trial of a suggested modification to permit of the neutralisation of the ammonia vapours disengaged from the still in an appropriate lead-lined seal pot fed with acid liquor continuously circulated from the washer, with diversion of the liberated foul gases—carbon dioxide, sulphuretted hydrogen, and hydrocyanic acid—to an oxide heap suitably placed outside the building.

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* See Thomas Holgate, *Journ. Gas Lighting*, August 30, 1904, p. 602.

Ammonia Solution.

The apparatus so far described is applied to the manufacture of ammonium sulphate. A German type of still for the production of ammonia solution ("aqua ammonia") is shown in Fig. 18. Milk of lime is introduced by the pump *D*

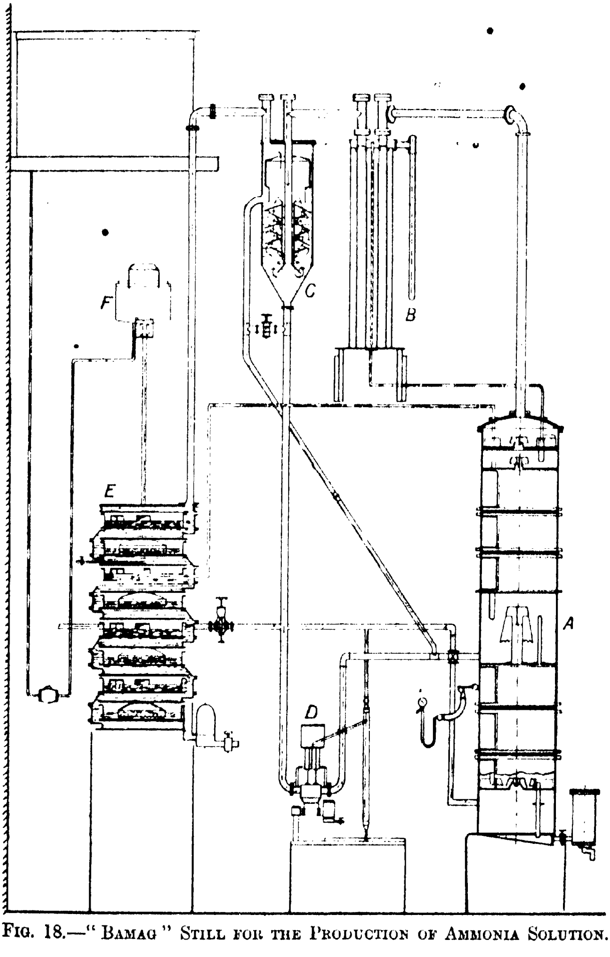

FIG. 18.—"BAMAG" STILL FOR THE PRODUCTION OF AMMONIA SOLUTION.

into a lower compartment, *A*, of the still, with a deep bubbler so that the liquid is effectively stirred. The milk of lime passes to the pump through a washer, *C*, in which the ammoniacal vapours from the top of the still are scrubbed free from sulphur compounds before passing to the absorber, *E*, in which they are brought into contact with water for absorption. The absorber is cooled by circulation of liquor passing to the still through three alternative feeds, as shown. *B* is a liquor preheater.

The Economics of Ammonia Recovery.

The cost of recovering ammonia during the carbonisation or gasification of coal, and of converting it into ammonium sulphate, will vary according to the particular industry selected and with the type of recovery process adopted.

A broad distinction may be drawn between those industries, such as the illuminating gas industry, in which crude ammonia liquor is recovered by water absorption and those in which the ammonia contained in gas is fixed directly in the form of sulphate by means of semi-direct or direct recovery processes.

Cost of Manufacture of Sulphate from Gasworks Liquor.

The Nitrogen Products Committee (Final Report, 1920, p. 230) deal only with "authoritative figures" of the pre-war costs involved in the manufacture of sulphate from crude ammoniacal liquor at a self-contained works making its own sulphuric acid, but purchasing the crude liquor.

Capital Costs.—The capital cost of the sulphuric acid plant amounts to about £1·75 per long ton of 70 per cent. acid per annum, or £1·92 per 1·1 tons of acid (the amount required to produce 1 ton of sulphate of ammonia).

The capital cost of the plant for working up the crude gasworks liquor and fixing the ammonia as sulphate amounts to about £4·5 per long ton of sulphate per annum.

The capital cost of the complete works would thus be £1·92 plus £4·5, equal to £6·42 in all, per ton of sulphate per annum.

Production Costs.—The cost of making the sulphuric acid may be placed at £1 per long ton, inclusive of all charges in respect of labour, materials, repairs, maintenance of the plant, and interest on capital.

The cost of working up the gas liquor and fixing the ammonia (exclusive of losses) is as follows:

	Sulphate per Long Ton.		
	£	s.	d.
Materials:			
1·1 tons of 70 per cent. sulphuric acid at £1	1	2	0
1·3 tons of fuel at 7s. 6d.	0	9	9
0·3 yard of lime at 10s.	0	3	0
Manufacturing costs, including labour, repairs, maintenance, general charges, and interest at 5 per cent.	1	7	0
..	£3	1	9

Note.—These figures do not include the cost of the crude liquor required per ton of sulphate manufactured, which (allowing for a loss, say, of 2 per cent. ammonia) would amount to about 14·7 tons of 8-ounce liquor (1·73 per cent. NH_3). The market price of such liquor itself would be based upon the market price of sulphate, which amounted (average 1911-1913) to £13 16s. 8d. per long ton (24·5 per cent. NH_3).

The cost of purchased sulphuric acid is given (*ibid.*, p. 13) at £1 10s. per long ton, presumably delivered at the consumer's works. Excluding the cost of gas liquor, and assuming purchase of acid at the above price, the lowest average cost of production of 1 long ton of sulphate at pre-war prices would thus be somewhere in the neighbourhood of £3·5 (£3 10s.).

In the Fifty-fourth Annual Report of the Chief Inspector of Alkali Works, 1917, Mr. David Vass, engineer and manager of the Corporation Gasworks at Perth, supplies figures relating to the manufacture of sulphate of ammonia for the years 1913 to 1918, which are presented in Table A. The cost for fuel is arrived at by taking a tenth part of the cost of the total fuel used in the boilers. The sulphate plant is supplied with steam from the same boilers, and a daily estimate is made of the total fuel consumed. All the other items, with the exception of depreciation, are actual outlays for sulphate alone. Depreciation is put in at a fixed sum of £62 10s. No sum is allowed for office management, rent of premises, etc., and similar landlord's charges, which would be applicable in the case of a private manufacturer.

Some of the figures supplied by Mr. Vass are presented in Table B (Works "C"), together with the average cost items for acid, fuel, lime, wages, and depreciation for the four years 1915 to 1918, to compare with similar figures relating to Works "A" and "B" in the Home Counties. In the latter case some of the figures—*e.g.*, for lime and fuel (Works "A") and of fuel (Works "B")—have had to be estimated. This, of course, somewhat detracts from their value, as the fuel item is undoubtedly an important factor in the manufacture of sulphate, and there is certainly room for economy in the fuel consumption at many of the smaller sulphate works.

In Table C are presented cost items relating to the "Direct" process at the largest and best conducted Works, "E."

In Table D the average cost items for the years 1915 to 1918 relating to the three Works, "A" and "B" (Table B) and Works "E" (Table C), are compared. It is interesting to note the relatively heavy cost for acid in all three works; that for labour is markedly higher in the case of Works "E," operating the "Direct" process—28 per cent. of the total, as against 17·5 and 17·0 per cent. respectively, for the older distillation process at Works "A" and "B," and 21·2 per cent. at Works "C" (Table A).

The By-Product Ammonia Industry.

The by-product ammonia industry may be regarded broadly as an outcome of the development of the illuminating gas and coke-oven industries, and its rapid expansion is indicated by the fact that during the period 1903 to 1913 the world's production of ammonia nitrogen increased to the extent of over 150 per cent. Just before the war this industry ranked almost equal in importance with the Chilean nitrate industry, for although the world's production of ammonia nitrogen was less than the output of nitrate nitrogen, the rate of increase in the former exceeded that of the latter.

The scale of the world's production during the years 1903 to 1919, and the corresponding average annual market prices in the United Kingdom, are set out in Table E. The whole output is there expressed as ammonium sulphate, though a portion of it was, of course, actually in the form of ammoniacal liquor.

TABLE A.—COST OF MAKING SULPHATE IN GASWORKS PER LONG TON (24½ PER CENT. NH_3): ORDINARY DISTILLATION PROCESS. (FRIARTON WORKS OF THE PERTH CORPORATION.)

	1913.	1914.	1915.	1916.	1917.	1918.	*Average for* 1915 *to* 1918.
Total sulphate made ..	250 tons	216 tons	225 tons	270 tons	276 tons	237 tons	252 tons
Materials:	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d. *Per Cent.*
Fuel (estimated) ..	0 5 4·32	0 6 5·89	0 6 8·59	0 7 8·16	0 10 1·66	0 14 11·27	0 9 9 (10·0)
Lime	0 1 8·16	0 1 10·91	0 1 3·61	0 1 2·08	0 2 2·01	0 1 1·85	0 1 5 (1·5)
Acid	1 12 1·34	1 12 10·75	2 0 9·89	3 10 1·81	3 12 0·53	3 13 6·46	3 4 11 (67·3)
Manufacturing Costs:							
Wages	0 15 4·26	0 17 9·27	0 16 1·80	0 17 2·64	0 17 7·98	1 10 9·26	1 0 6 (21·2)
Bags and twine ..	0 0 4·03	0 0 1·90	0 0 2·57	0 0 4·49	0 2 5·47	0 5 8·67	4 16 7 (100·0)
Depreciation.. ..	0 5 0·00	0 5 9·54	0 5 6·73	0 4 7·55	0 4 6·25	0 5 3·34	
Registration fees ..	0 0 2·88	0 0 3·34	0 0 3·19	0 0 2·67	0 0 2·60	0 0 3·04	
Sundries (including subscriptions to S/a Association) ..	0 0 7·93	0 2 1·66	0 5 7·86	0 5 10·10	0 9 1·12	0 10 3·33	
Total ..	3 0 9	3 7 5	3 16 8	5 7 3	5 18 4	7 1 11	
Market value of crude liquor f.o.r. at gasworks, calculated per ton S/a	3 6 8	3 0 0	5 0 0	5 6 8	5 6 8	5 6 8	
Total cost of S/a as made	6 7 5	6 7 5	8 16 8	10 13 11	11 5 0	12 8 7	
Average price received for S/a	12 7 9	12 7 6	16 2 5	15 5 9	15 6 7	17 3 10	
"Profit" made in S/a house	6 0 4	6 0 1	7 5 9	4 11 10	4 1 7	4 15 3	

TABLE B.—COST OF MAKING SULPHATE IN GASWORKS : ORDINARY DISTILLATION PROCESS.

	Cost per Long Ton of Sulphate made (24½ per Cent. NH_3).						
	1913.	1914.	1915.	1916.	1917.	1918.	*Average* 1915 *to* 1918.
Total sulphate made	178 tons	168 tons	157 tons	126 tons	169 tons	177 tons	157 tons
Materials:	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Acid	2 2 7	2 2 10	3 4 5	3 3 9	3 1 5	3 11 7	3 5 6
Fuel (estimated at 29 tons coke per month)	1 2 6	1 3 9	1 18 2	2 7 7	1 19 8	2 0 8	2 1 0
Lime (estimated)	0 5 10	0 5 7	0 3 7	0 5 10	0 5 8	0 7 10	0 5 8
Manufacturing costs:							
Wages	0 11 11	0 12 6	0 13 6	0 17 5	1 2 3	2 1 1½	1 4 8
Repairs	0 3 11	0 3 7	0 4 10	0 5 6	0 1 9	0 2 3	6 16 10 0 3 5
Interest and depreciation on plant (£300) and buildings (£150) at 5 per cent. on prime cost ..	0 2 6	0 2 8	0 2 10	0 3 7	0 2 7	0 2 6	0 2 10
Works "A" Total ..	4 9 3	4 10 11	6 7 4	7 3 8	6 13 4	8 6 9	7 3 1

TABLE B (*Continued*).—COST OF MAKING SULPHATE IN GASWORKS: ORDINARY DISTILLATION PROCESS.

	Cost per Long Ton of Sulphate made (24½ per Cent. NH_3).						
	1913.	1914.	1915.	1916.	1917.	1918.	*Average* 1915 *to* 1918.
Total sulphate made	112 tons	—	135 tons	131 tons	134 tons	128 tons	132 tons
Materials:	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Acid	2 18 10	—	2 15 4	5 4 1	7 8 10	7 1 8	5 12 1
Fuel (estimated)	0 11 1	—	0 13 9	0 14 10	0 15 9	0 19 2	0 15 10
Lime	0 0 10	—	0 1 7	0 1 8	0 3 3	0 5 6	0 3 0
Manufacturing Costs:							
Wages	1 0 6	—	1 2 1	1 3 7	1 6 2	1 16 9	1 7 1
							7 18 0
Repairs, interest, and depreciation on plant (£300)	0 10 8	—	0 8 10	0 9 0	0 8 11	0 9 5	0 9 1
Works "B" Total ..	5 1 11	—	5 1 7	7 13 2	10 2 11	10 12 6	8 7 1
Total sulphate made	250 tons	216 tons	225 tons	270 tons	276 tons	237 tons	252 tons
Materials:	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Acid	1 12 1	1 12 11	2 0 10	3 10 2	3 12 1	3 13 6	3 4 11
Fuel (estimated at one-tenth total fuel consumed at boiler)	0 5 4	0 6 6	0 3 9	0 7 8	0 10 2	0 14 11	0 9 9
Lime	0 1 8	0 1 11	0 1 4	0 1 2	0 2 2	0 1 2	0 1 5
Manufacturing Costs:							
Wages	0 15 4	0 17 9	0 16 2	0 17 3	0 17 8	1 10 9	1 0 6
							4 16 7
Depreciation, taken as fixed charge, £62 10s.	0 5 0	0 5 9	0 5 7	0 4 8	0 4 6	0 5 3	0 4 11
Works "C" Total ..	2 19 5	3 4 10	3 10 8	5 0 11	5 6 7	6 5 7	5 1 6

TABLE C.—COST OF MAKING SULPHATE IN GASWORKS: "DIRECT" PROCESS.

Works "E."	*Cost per Long Ton of Sulphate made (24½ per Cent. NH_3).*				
	1915.	1916.	1917.	1918.	*Average,* 1915 *to* 1918.
Total sulphate made ..	110 tons	95 tons	117 tons	126 tons	112 tons
Materials:	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Acid	1 15 8	4 5 10	5 3 6	5 14 2	4 4 9
Fuel (one-tenth of coke used on boilers) ..	0 6 8	0 10 8	0 8 5	0 8 11	0 8 8
Lime	0 3 6	0 5 6	0 6 9	0 10 0	0 6 5
Manufacturing Costs:					
Wages	1 8 10	2 1 5	1 15 6	2 10 0	1 19 2
Repairs, interest on plant, etc. ..	Not stated	—	—	—	—
	—	—	—	—	6 19 0

TABLE D.—COMPARATIVE COST OF MATERIALS AND LABOUR IN MANUFACTURE OF SULPHATE BY THE ORDINARY DISTILLATION AND "DIRECT" PROCESSES: AVERAGE COST, 1915 TO 1918.

	Ordinary Distillation Process.				*"Direct" Process.*	
	Works "A," Middlesex.		*Works "B," Herts.*		*Works "E," Herts.*	
	Per Long Ton of Sulphate.	*Per Cent. of Total Cost.*	*Per Long Ton of Sulphate.*	*Per Cent. of Total Cost.*	*Per Long Ton of Sulphate.*	*Per Cent. of Total Cost.*
Total sulphate made	157 tons		132 tons		112 tons	
Materials & Wages:	£ s. d.		£ s. d.		£ s. d.	
Acid	3 5 6	48·0	5 12 1	71·0	4 4 9	61·0
Fuel (estimated)	2 1 0	30·5	0 15 10	10·0	0 8 8	6·5
Lime	0 5 8	4·0	0 3 0	2·0	0 6 5	4·5
Wages	1 4 8	17·5	1 7 1	17·0	1 19 2	28·0
Total ..	6 16 10	100·0	7 18 0	100·0	6 19 0	100·0

The price in column 4 of Table E refers to a product containing 24 per cent. of ammonia for the period 1910-1913, and 24·5 per cent. for 1914-1919.

TABLE E.—WORLD'S PRODUCTION OF AMMONIUM SULPHATE.

Year.	*Production of Ammonia Nitrogen.*		*Average Annual Market Price of Ammonia Nitrogen as Sulphate.*			
	Ammonium Sulphate.	*Combined Nitrogen on Basis of 25 per Cent.* NH_3.	*Sulphate (24 to 24½ per Cent.* NH_3*) f.o.b. U.K. Ports, per Long Ton of Product.*			*Combined Nitrogen on Basis of 25 per Cent.* NH_3*, per Metric Ton of Nitrogen.*
	Long Tons.	*Metric Tons.*	£	s.	d.	*Pounds.*
1903	540,200	112,900	12	9	[illegible]	59·55
1904	594,500	124,250	12	3	8	58·23
1905	640,900	133,940	12	10	9	59·93
1906	716,100	149,660	12	0	9	57·54
1907	895,320	187,120	11	15	8	56·32
1908	858,000	179,320	11	12	0	55·44
1909	978,000	204,400	11	5	0	53·77
1910	988,579	202,560	12	3	2	60·40
1911	1,079,364	221,161	13	15	3	68·40
1912	1,212,556	248,453	14	7	9	71·50
1913	1,381,827	283,136	13	7	8	66·50
1914	1,186,741	243,163	11	7	1	55·40
1915	1,173,091	240,366	14	8	1	70·30
1916	1,202,548	246,402	16	0	0	78·10
1917	979,436	200,686	17	17	0	87·10
			15	18	0*	77·50
1918	1,118,620	229,205	23	2	11	112·90
			17	7	6*	84·80
1919	1,466,000	300,383	26	12	6	130·00
			20	6	6*	99·20

The figures given in Table F give the production of ammonium sulphate by individual countries for the years 1911 to 1919. The quantities in both Table E and Table F should be regarded as approximate only.

The German figures for the war period probably represent sulphate used as fertiliser only. The figures for the United Kingdom refer to actual sulphate.

About 70 per cent. of the total output of ammonia nitrogen was therefore produced by Germany and the United Kingdom alone.

It should be noted in passing that in 1913 the coke-oven industry was responsible for 86 per cent. of the total German production, and for 78 per cent. of the total output of the United States, as compared with 30 per cent. in the case of the

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* Home.

TABLE F.—NATIONAL PRODUCTION OF AMMONIUM SULPHATE.

Country.	Quantities in Metric Tons.								
	1911.	1912.	1913.	1914.	1915.	1916.	1917.	1918.	1919.
Germany	418,000	492,000	548,558	488.625	341.308	341,270	281,600	262,700	660,431
United Kingdom ..	391,135	394,521	439,565	432,835	445.029	432,836	250,000	262.140	356,745
United States ..	115.245	149,700	176.900	166.016	226,834	294.838	335,701	352,406	383.763
France	62.000	69,100	74,500	—	42.000	25,000	34.000	30.000	45.000
Belgium	40,700	43.700	53,600*	5.000	5.000	4,000	—	—	—
Japan	—	—	—	16.035	31.824	38.203	57.915	91,444	—
Spain	—	—	—	16.000	16.500	18.000	12,750†	—	—
Australia	—	—	—	5.741	6.503	7,214	9.988	12.000	—
Other countries‡ ..	171.283	107,700	123.200	—	—	—	—	—	—
Total ..	1,198.363	1,256,721	1,416,323	1,130.252	1.114.998	1.161,361	981,954	1,010,690	1,445,939

The war figures for U.S.A. and Japan are particularly noteworthy.

Statistics for 1911 from "Production et Consommation des Engrais Chimiques dans le Monde," Institut International d'Agriculture, Rome, 2nd edition, 1914; and for 1912 and 1913 from *Monthly Bulletin of Agricultural Intelligence and Plant Diseases*, International Institute of Agriculture, Rome, Year VI., No. 3, March, 1915; also from Annual Reports of the Chief Inspector of Alkali Works. Recent figures from "International Movements of Fertilisers," Rome, 1920.

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* With Holland from 1912. † Nine months. ‡ These figures include some round-figure estimates.

United Kingdom ("International Crop Report and Agricultural Statistics," International Institute of Agriculture, Rome, vol. vii., No. 9, September, 1916; also Alkali Inspector's Report for 1913).

Consumption.

The following figures have been given for the world's consumption of ammonium sulphate from 1912 onwards (Table G).

TABLE G.—WORLD'S CONSUMPTION OF AMMONIUM SULPHATE.

Country.	*Quantities in Metric Tons.*			
	1912.	1913.	1914–1918.	1919.
Germany	425,000	460,000	Figures not available.	508,000
United States	250,139	266,850		304,500
Japan	87,000	115,000		152,000
United Kingdom	91,444	98,557		264,000
France	90,000	97,000		81,200
Spain and Portugal ..	45,000	75,000		83,200
Java	57,000	68,000		71,000
Belgium	42,000	45,700		40,600
Italy	29,500	33,000		30,500
Austria-Hungary	13,000	16,000		?
Netherlands	8,000	8,000		10,200
Egypt	1,650	2,000		1,000
Sweden	1,300	1,350		1,370
Denmark	70	300		300
West Indies and Demarara				12,200
Mauritius				6,100
Australia				2,030
Total ..	1,141,103	1,286,757		1,568,200

About 60 per cent. of the total pre-war consumption was therefore accounted for by the requirements of Germany and the United States alone.

In Table H are given figures with specific reference to the British pre-war industry. The figures are inclusive of all forms of ammoniacal compounds, such as ammonia liquor and ammonium salts, expressed in terms of ammonium sulphate (Final Report, Nitrogen Products Committee, 1920, and Statistical Supplement, 1921).

The table on pp. 126 and 127 reveals a number of striking facts, which may be summarised as follows:

TABLE II.—BRITISH PRE-WAR PRODUCTION, EXPORTS,

(Expressed in Terms of Ammonium

Source and Disposal.	1903.	1904.	1905.	1906.	1907.	1908.	1909.
Production:							
Gasworks	149,489	150,208	155,975	157,160	165,474	165,218	164,276
Ironworks	19,119	19,568	20,376	21,284	21,024	18,131	20,228
Shale works	37,353	42,486	46,344	48,534	51,338	53,628	57,048
Coke-oven works ..	17,438	20,848	30,732	43,677	53,572	64,227	82,886
Producer gas and carbonising works (bone and coal)	10,265	12,880	15,705	18,736	21,873	24,024	24,705
Total:							
As sulphate (long tons)	233,664	245,990	269,114	289,391	313,281	325,228	349,143
As combined nitrogen (metric tons) ..	47,900	50,420	55,160	59,320	64,220	66,670	71,570
Exports:							
As sulphate (long tons)	162,300	177,280	189,350	201,500	230,000	235,000	264,000
As other products expressed as sulphate..	—	—	—	—	—	—	—
As combined nitrogen (metric tons) ..	33,270	36,340	38,810	41,300	47,150	48,170	54,120
Estimated home consumption for all purposes (including fertiliser:							
As sulphate (long tons)	71,700	68,500	68,000	82,000	87,500	83,000	87,000
As combined nitrogen (metric tons) ..	14,690	14,040	13,940	16,810	17,930	17,010	17,830
Estimated use for fertiliser (long tons) ..	—	—	—	—	—	—	—
Estimated use as combined nitrogen (metric tons)	—	—	—	—	—	—	—

(From the Final Report of the Nitrogen Products

AND CONSUMPTION OF AMMONIA NITROGEN.

SULPHATE, 24·5 PER CENT. NH_3.)

1910.	1911.	1912.	1913.	1914.	1915.	1916.	1917.	1918.	1919.
167,820 20,139 59,113 92,665	168,783 20,121 60,765 105,343	172,094 17,026 62,207 104,932	182,180 19,956 63,061 133,816	175,930 16,008 62,749 137,430	173,675 15,142 58,826 145,406	172,269 15,154 57,988 159,506	188,478 13,621 60,560 166,354	173,541 12,717 58,311 164,448	173,50 10,87 48,61 144,36
27,850	29,964	32,049	33,605	34,295	33,218	28,786	29,604	23,534	20,15
367,587	384,976	388,308	432,618	426,412	426,267	433,703	458,617	432,551	397,51
75,350	78,920	79,600	88,680	87,410	87,380	88,880	93,980	88,640	81,46
284,000	292,000	287,000	323,000	313,341	293,853	259,290	62,931	19,150	94,43
—	—	—	14,000	12,000	14,000	15,000	12,000	8,000	17,60
68,220	59,860	58,830	69,100	66,600	63,100	56,100	15,400	5,700	23,00
87,000	85,500	90,000	97,000	101,000	118,000	160,000	384,000	404,000	285,500
17,830	17,520	18,450	19,880	20,700	24,200	32,800	78,700	82,900	58,600
—	—	—	60,000	—	—	80,000	230,000	234,000	269,000
—	—	—	12,000	—	—	16,000	46,000	47,000	54,000

Committee, 1920; and Statistical Supplement to same, 1921.)

(*a*) The total British production of ammonia nitrogen in 1913 was practically double the production in 1903. It has decreased somewhat since 1913.

(*b*) Of the producing industries, the recovery coke-oven industry has shown a remarkable expansion, the output of by-product ammonia from this source in 1913 being nearly eight times the output in 1903, and amounting to over 30 per cent. of the total production. The maximum production from this source was in 1917; since then it has decreased.

(*c*) The gasworks industry, which occupied an outstanding position in 1903 and accounted for nearly 65 per cent. of the total output of ammonia nitrogen in that year, exhibited a steady expansion, with an increased output of 20 per cent., in 1913. Since 1913 the supply has steadily declined, with the exception of the year 1917. In consequence of the development of the other by-product industries, this output represented about 40 per cent. of the total in 1913. In 1919 the percentage was about 42, since the total production had declined to 92 per cent. of that in 1913.

(*d*) In the case of the smaller by product industries, the output from producer-gas and carbonising works had trebled in 1913, from which date it has steadily diminished; while that from shale works, which had nearly doubled in 1913, has also steadily declined since that date. The output from ironworks during the period 1903 to 1913 remained stationary, but declined considerably in the period 1913 to 1919.

(*e*) The British exports of ammonium sulphate in 1913 were double those in 1903, accounting for over 75 per cent. of the total production, as compared with nearly 70 per cent. in 1903. In 1919 the exports had fallen to about 30 per cent. of their value in 1913; the exports in 1919 represented only about 18 per cent. of the total production.

(*f*) The estimated home consumption for all purposes, although showing a steady expansion, was only 35 per cent. greater in 1913 than in 1903, representing about 22 per cent. of the total production in 1913. The home consumption for all purposes in 1919 was over 70 per cent. of the total production.

The extension of the coke-oven industry during the war period, consequent upon the augmented production of iron and steel, was accompanied by a substantial increase in the output of by-product ammonia, more particularly in Germany and the United States.

Market Prices.

The market price of ammonia nitrogen depends upon the precise form in which it is placed on the market. The more important forms in which by-product ammonia is utilised commercially are as follows: Crude gasworks liquor (*i.e.*, 8 to 10 ounce liquor, equivalent to 1·73 to 2·17 per cent. NH_3); concentrated gas liquor containing 15 to 20 per cent. of NH_3; pure ammonia liquor or spirit containing from 20 to 35·6 per cent. NH_3 (sp. gr. 0·88); anhydrous liquid ammonia; and ammonium sulphate. The figures given below deal with the corresponding market prices of ammonia nitrogen on the basis of long tons.

1. Crude gasworks liquor of 8-ounce strength, containing 1·73 per cent. NH_3 could be purchased prior to the war for about 14s. per ton delivered, corresponding to £40·46 per ton of actual NH_3 in the form of 8 ounce liquor.

2. Concentrated gas liquor containing, say, 14 to 17 per cent. NH_3 could be purchased during 1911 to 1913 for an average price of about 9s. 3d. per unit (1 per cent. NH_3) per ton delivered, corresponding to, say, £7·4 per ton of 16 per cent. liquor, or £46·25 per ton of actual NH_3 in the form of 16 per cent. liquor.

3. Pure ammonia spirit (20 to 25 per cent. NH_3) could be purchased under pre-war conditions for an average price of about 10s. 3d. per unit per ton at the maker's works, corresponding to £12·81 per ton of spirit (25 per cent. NH_3), or £51·25 per ton of actual NH_3 in the form of pure spirit.

4. Anhydrous liquid ammonia was worth about 1s. per pound prior to the war, or about £112 per ton.

5. The pre-war market price of ammonium sulphate in this country (average 1911–1913) was £13 16s. 8d. (£13·83) per ton, calculated upon a content of 25 per cent. NH_3 (nominally 24 per cent.), equivalent to £13·61 per metric ton, £54·44 per metric ton of ammonia in the form of ammonium sulphate (25 per cent. NH_3), or £66·10 per metric ton of combined nitrogen in the same form.

The selling price of ammonium sulphate fluctuated considerably in this country during the war period, varying from £14·4 per ton in 1915 to £17·23 per ton in the early months of 1916. In the latter part of 1916 the price was fixed by a Government Committee at £15, and subsequently at £15·5, per ton at the works, and early in 1917 the price was fixed at £15·5 per ton at the works and at £16 delivered.

The last-mentioned figure is equivalent to £64 per long ton of ammonia in the form of sulphate (25 per cent. NH_3), £62·98 per metric ton, or £76·45 per metric ton of combined nitrogen in the same form.

The lowest recorded price of ammonium sulphate in this country (in 1897) was £7·5 per long ton, equivalent to £7·38 per metric ton, or £35·84 per metric ton of combined nitrogen in the form of sulphate (25 per cent. NH_3).

By far the largest proportion of the ammonia nitrogen produced in this country is fixed in the form of ammonium sulphate. The market price of sulphate has hitherto been based upon a quality termed "grey," containing 24 per cent. NH_3, but the custom of the trade is to supply a product containing 24·5 per cent. NH_3, while a standard of 25 per cent. NH_3 appears to be coming into vogue.

The usual method of arriving at the market price of ammonia in the form of crude liquor is to make certain deductions from the market price of sulphate f.o.b. an English port. These deductions are as follows: 3·5 per cent. of the price of sulphate, representing brokerage and commission for marketing, and a further sum of the order of £3 per ton of sulphate, representing the pre-war cost of converting ammonia into sulphate, inclusive of the cost of acid, labour, packages, and so on. In the case of sulphate containing 25 per cent. NH_3, the balance after these deductions have been made represents the market price of 25 units of ammonia (0·25 ton) in the form of crude liquor.

Applying the above method to pre war market prices of sulphate assumed to contain 25 per cent. NH_3, the following figures are obtained:

(*a*) With sulphate at the pre-war (average 1911-1913) price of £13·83 per ton, the market price of 0·25 ton NH_3 in the form of crude liquor would be £10·35, equivalent to £41·4 per ton of ammonia.

(*b*) With sulphate at the lowest known market price in this country (in 1897)—namely, £7·5 per ton—the market price of 0·25 ton of NH_3 in the form of crude liquor would be £4·24, equivalent to £16·96 per ton of ammonia.

In consequence of the abnormal price of sulphuric acid and of the cost of labour and fuel under war conditions, the method of deduction referred to above cannot be relied upon to give a fair indication of the market price of crude ammonia liquor as such during the war period.

Table I* gives the pre-war market price of ammonia and of ammonium sulphate, from which it appears that the pre-war market price of a ton of ammonia in the form of pure spirit (20 to 25 per cent. NH_3) represented an addition of the order of £10 to £11 to the market price of ammonia in the form of crude liquor.

TABLE I.—PRE-WAR PRICES OF AMMONIA AND AMMONIUM SULPHATE.

Product.	*Actual NH_3 in Form of Product Specified.*		*Combined Nitrogen in Form of Product Specified.*
	Pounds per Long Ton.	*Pounds per Metric Ton.*	*Pounds per Metric Ton.*
Crude gasworks liquor (1·73 per cent. NH_3) delivered	40·46	39·81	48·33
Concentrated gas liquor (16 per cent. NH_3) delivered (average 1911-1913)	46·25	45·51	55·25
Pure ammonia spirit (20 to 25 per cent. NH_3), at maker's works	51·25	50·43	61·22
Anhydrous liquid ammonia ..	112·00	110·21	133·78
Ammonium sulphate (25 per cent. NH_3) at pre-war (average 1911-1913) price f.o.b.	55·33	54·44	66·10
Ammonia in form of crude liquor based on price of sulphate:			
(*a*) Pre-war (average 1911-1913)	41·40	40·74	49·45
(*b*) Lowest known	16·96	16·69	20·26

* From Final Report of Nitrogen Products Committee.

On the withdrawal of the subsidy on sulphate of ammonia, the Board of Agriculture and Fisheries agreed with the makers on the following maximum prices for home agricultural use:

	Month of Delivery.	*Price per Ton in Bags, Net Cash.*		
		£	s.	d.
1919	October	20	0	0
	November	20	15	0
	December	21	0	0
1920	January	21	7	6
	February	21	15	0
	March, April, May	22	2	0

In July, 1921, the British Sulphate of Ammonia Federation fixed prices for home agricultural use at £14 6s. per ton of dry neutral quality on a basis of 27·75 per cent. ammonia, and £13 3s. for ordinary quality on a basis of 25·25 per cent. ammonia. In January, 1922, the latter price had been advanced to £15.

Economic Considerations.

Under pre war conditions the export trade of the United Kingdom in ammonium sulphate was larger than that of any other country in the world. During the period 1911 to 1913 about three-quarters of the total home production was disposed of in this way, amounting to over 60,000 metric tons of ammonia nitrogen per annum. The trade was maintained during the years 1914 to 1916, but practically ceased in 1917, owing to the increasing demands for munitions and fertilisers.

Two of the largest customers of Great Britain before the war were the United States and Japan, but these countries have now developed their own nitrogen resources to such an extent that the loss of these markets must be regarded as certain. On the other hand, it is possible that the enhanced appreciation of the value of the nitrogenous fertilisers which the war has brought about may cause a greatly extended use of ammonium salts in countries where their applicability has, up to the present been limited by war conditions.

Such countries as India, Africa, and South America constitute in this respect potential markets for large quantities of ammonium sulphate. In order that the position of the

United Kingdom in foreign markets may be maintained, it is essential that every method possible should be adopted for lowering the production and transportation costs of nitrogenous fertilisers. In the case of ammonium sulphate it should be remembered that about 1 ton of chamber sulphuric acid is needed for the production of 1 ton of product, and even when cheap acid is available and the manufacture is carried out on a large scale, it has been stated that the cost incurred by the by-product industry merely for fixing the ammonia as sulphate and preparing the solid product for the market may amount to £2·5 to £3 per long ton of sulphate.

The national interests demand that an abundant and cheap supply of fertilisers should be available, not only for the agricultural requirements of the United Kingdom, but also for export to other food producing countries. This end, however, cannot be served by measures which limit the production of the cheap by-product acid, which has already conferred advantages upon other countries. Failing a cheaper acid from existing or potential sources, a solution of the problem of reducing the cost of fixing ammonia must be sought in methods which avoid the use of sulphuric acid (see p. 157).

After a full consideration of the future prospects of the export trade in nitrogenous fertilisers in the light of the evidence that has been given, the Nitrogen Products Committee is of the opinion that the outlook is undoubtedly favourable. The diversion of a large proportion of the world's production of fixed nitrogen to munitions for a period of several years has been to the great detriment of the world's supply of food and in many countries the scale of subsistence has been reduced far below the pre-war level. The vital importance of nitrogenous manures has received almost universal recognition, and, in view of the leeway to be made up, there is certain to be a large increase in the consumption in the near future, especially in countries which have been unable to obtain supplies of ammonium sulphate from Great Britain or elsewhere during the war. The conditions will undoubtedly be unsettled for a time, but, in the judgment of the Committee, the demand in external markets will be more than adequate for the absorption of ammonium sulphate on the pre-war scale of exportation. The extent to which the markets are retained by British producers, however, must depend upon their ability to compete on favourable terms with other exporting countries.

TABLE J.—EXPORTS (PRODUCE AND MANUFACTURE OF U.K.).

	Sulphate of Ammonia (Tons), Seven Months ended July 31.			*Value in £, Seven Months ended July 31.*		
	1917.	1918.	1919.	1917.	1918.	1919.
To—						
France	8,249	3,042	6,493	155,647	66,879	142,673
Spain and Canaries	5,015	-	4,385	89,865	-	152,147
Italy	1	1,851	2,429	57	45,671	83,085
Dutch East Indies	6,480		2,488	119,618	-	64,447
Japan	4,050	-	2,188	72,882	-	37,144
United States ..	1,513			27,177	-	-
British West Indies	3,223	747	2,525	61,898	23,528	74,287
Other Countries	10,851	1,111	6,861	197,271	25,396	208,475
Total ..	39,385	6,751	27,369	727,445	161,474	762,258

The Uses of Ammonia and Ammonium Sulphate.

The requirements of ammonia nitrogen for industrial purposes are mainly in connection with the manufacture of ammonium salts, such as the carbonate and chloride, of cyanides by processes involving the use of alkali metals or salts, of sodium carbonate by the ammonia-soda process, of cellulose products and waterproofing preparations by means of the cuprammonium process, and for the refrigeration industry and the like.

There is no doubt, however, that the major portion of the output of the by-product ammonia industry was utilised in the form of ammonium sulphate as a fertilising material. There has always been a certain amount of prejudice against the use of this salt for such a purpose, and this has not been without foundation on account of the impure character of the product and of its acidity, the latter having a deleterious action in the soil and a destructive effect upon the bags in which the sulphate is marketed. The attention of the manufacturers had been directed before the war to the need for improvement in these directions, and processes had been devised for the remedy of the evils. Owing, however, to the fact that the sulphate is readily absorbed by the soil and is not easily washed out even by tropical rainfall, and also that it does not give rise to toxic products or suffer loss under anaërobic conditions, it is largely used in preference to Chile nitre in tropical and subtropical countries such as Java and Japan. There has been a substantial increase in the output of by-product ammonia during the war period, principally from works engaged in the manufacture of metallurgical coke, and the maintenance or extension of this output will, of course, depend upon the future demands for ammonia nitrogen, and the competitive price of other nitrogenous fertilisers.

Ammonium Sulphate in Agriculture.

The employment of ammonium sulphate in agriculture since the commencement of the war had been greatly extended, owing to the diversion of the supplies of Chile nitrate to the explosives industry. While it is unlikely that the present scale of consumption will be maintained in countries producing by-product ammonia when competing supplies of Chile nitrate and other fertilisers again become available, nevertheless there is reason to believe that the future demand for sulphate will be in excess of the pre-war requirements.

Experiments have been conducted at Rothamsted for many years past on the effect of nitrogenous manures in improving agricultural yields.

Systematic records have been kept with regard to wheat production for a period of some seventy to eighty years (see Hall, "Rothamsted Experiments," 1917). A brief résumé of the experiments on wheat may be given, as showing the importance of nitrogenous fertilisers in relation to food production.

The chief difficulty in growing wheat continuously is that of keeping the land clean. Weeds tend to accumulate from year to year, and the fact that the crop is in occupation of the ground for the greater part of the year leaves little opportunity for cleaning operations. The usual practice is to scuffle the land immediately after the harvest, the weeds being removed. The land is then ploughed 5 or 6 inches deep. Mineral and other autumn-sown manures are sown and harrowed in, after which the seed is drilled.

The experiments were originated just about the time when Liebig advanced the theory that it was only necessary to supply a plant with the mineral constituents left as ash when the plant is burnt. The carbon and nitrogen required in its assimilation processes were supposed to be drawn directly from the atmosphere.

The first experiments, therefore, were designed to test this statement, and were gradually extended to include the gathering of information concerning other individual mineral constituents. The long duration of the experiments serves to make them very authoritative, as irregularities, such as the attacks of insect and other pests and climatic variations, can be eliminated.

Table K (p. 137) gives the nature and quantities of the manures applied each year to the various plots at Rothamsted.

It is understood that "mineral manures" include phosphates, potash, magnesia, soda, and other constituents left as ash when the plant is burnt, but not any manure containing nitrogen. These manures are sown before the seed in autumn, rape cake and farmyard manure and some of the ammonium salts also being applied in autumn before seeding; but the nitrate of soda and the majority of the ammonium salts are applied as top dressings in the spring.

The ammonium salts consist of equal parts of ammonium sulphate and ammonium chloride; 200 pounds of this are equivalent to 43 pounds of nitrogen, which is that contained in 275 pounds of sodium nitrate, or 1,889 pounds of rape cake.

Table L (p. 139) shows the average production of grain and straw for a period of sixty one years. The yield of grain is expressed as bushels per acre, and straw (including chaff) as hundredweights per acre.

During the last thirty years the crop from the unmanured plot has been practically constant. It has not received manure of any description since 1839, and appears to have reached a stationary condition, with an average crop of some 12½ bushels.

This crop will remove some 17 pounds of nitrogen, 9 pounds of phosphoric acid, and 14 pounds of potash, per acre per annum. There may also be a further loss of some 10 pounds of nitrogen per acre per annum in the drainage water, and also some may be removed in weeds. On the other hand, there may be a gain in nitrogen of some 5 pounds per annum, due

TABLE K.—EXPERIMENTS ON WHEAT, BROADBALK FIELD: MANURING OF THE PLOTS PER ACRE PER ANNUM, 1852, AND SINCE.

Plot.	*Abbreviated Description of Manuring.*	*Farmyard Manure.*	*Nitrogenous Manures.*			*Mineral Manures.*			
			Rape Cake.	*Nitrate of Soda.*	*Ammonium Salts.*	*Superphosphate.*	*Sulphate of Potash.*	*Sulphate of Soda.*	*Sulphate of Magnesia.*
		Tons	Lb.	Lb.	Lb.	Cwt.	Lb.	Lb.	Lb.
2	Farmyard manure	14						-	-
3	Unmanured								-
5	Minerals					3·5	200	100	100
6	Single ammonium salts and minerals		-		200	3·5	200	100	100
7	Double ammonium salts and minerals				400	3·5	200	100	100
8	Treble ammonium salts and minerals				600	3·5	200	100	100
9	Single nitrate and minerals			275		3·5	200	100	100
10	Double ammonium salts alone				400		-	-	-
11	Double ammonium salts and superphosphate ..				400	3·5	-	- -	-
12	Double ammonium salts and sulphate of soda ..				400	3·5		366·5	
13	Double ammonium salts and sulphate of potash ..				400	3·5	200		
14	Double ammonium salts and sulphate of magnesia				400	3·5			280
15	Double ammonium salts, in autumn, and minerals ..				400	3·5	200	100	100
16	Double nitrate and minerals			550		3·5	200	100	100
17	Minerals alone, or double ammonium salts alone, in alternate years					3·5	200	100	100
18					400				
19	Rape cake alone		1889						

to rain salts, the seed also supplying perhaps 2 pounds. There is thus a net loss of some 20 pounds of nitrogen per acre per annum.

Analyses on the soil indicate that there is a steady loss on the amount of combined nitrogen present in the soil, but in 1893 there were still over 2,500 pounds per acre in the top 9 inches of soil, so that an enormous reserve still remains to be tapped. With regard to mineral constituents, there are no external sources for the renewal of potash and phosphates, but the reserve in the soil is very great, amounting in 1893 to about 3,000 pounds of phosphoric acid and as much as 50,000 pounds of potash in the top layer of soil.

It is interesting to note that on a plot receiving no manure at all, although the yield is small, the grains of corn are individually almost of average size and quality. Starvation has the effect of diminishing the number but not the quality of the seed. The proportion of corn to straw is also high, indicating that starvation has resulted in the concentration of as much material as possible on the reproductive parts of the plant.

With regard to the plot of ground No. 2, treated with farmyard manure, there has here been a yearly dressing of some 14 tons per acre. The composition of the manure is very variable, but it is estimated that about 200 pounds of nitrogen, 78 pounds of phosphoric acid, and 235 pounds of potash, have been supplied on the average each year.

An average crop, however, will have removed only about 52 pounds of nitrogen, 27 pounds of phosphoric acid, and 53 pounds of potash, per acre per annum. In consequence, the yield from this plot has been increasing, particularly over the period between 1872 and 1881, which was, on the whole, fairly dry. Analyses show that enormous reserves of plant food have been accumulated in the soil of this plot, the amount of nitrogen in the surface soil being more than double that of the unmanured plot. There is evidence, however, that it would be impossible to crop these reserves out entirely, even over a long period, if corn were grown without further manure.

On Plots 6 and 7 artificial manures were applied, containing nitrogen, potash, and phosphoric acid, but without organic matter to form humus. Plot 7, over a period of forty years, showed no evidence of declining fertility, and the yield obtained from it was very little inferior to that obtained from the plot manured with farmyard manure. To this ground 86 pounds of nitrogen per acre were applied, of which the crop removed an average of 50 pounds. The phosphoric acid and potash supplied were also in excess of the requirements of the crop.

TABLE L.—EXPERIMENTS ON WHEAT, BROADBALK FIELD: PRODUCE OF GRAIN AND STRAW PER ACRE. AVERAGE OVER SIXTY-ONE YEARS (1852-1912), AND OVER TEN YEARS (1903-1912): ALSO PRODUCE IN 1911.

Plot.	*Abbreviated Description of Manuring.*	*Dressed Grain.*			*Straw.*		
		Average, 61 Years (1852-1912).	*Average, Last 10 Years (1903-1912).*	*Season 1911.*	*Average, 61 Years (1852-1912).*	*Average, Last 10 Years (1903-1912).*	*Season 1911.*
		Bush.	*Bush.*	*Bush.*	*Cwt.*	*Cwt.*	*Cwt.*
2	Farmyard manure.. ..	35·2	32·8	35·2	34·8	38·2	36·9
3	Unmanured	12·6	10·0	12·5	10·3	9·3	9·8
5	Minerals	14·5	12·5	14·8	12·1	11·9	12·8
6	Single ammonium salts and minerals	23·2	19·0	17·2	21·4	20·7	17·9
7	Double ammonium salts and minerals	32·1	27·9	25·6	32·9	32·3	27·6
8	Treble ammonium salts and minerals	36·6	33·8	36·4	41·1	42·1	35·7
9	Single nitrate and minerals	-	26·0	29·9	- -	28·7	29·0
10	Double ammonium salts alone	20·0	16·3	22·8	18·4	16·7	17·2
11	Double ammonium salts and superphosphate ..	22·9	17·1	20·1	22·3	20·2	15·2
12	Double ammonium salts and sulphate of soda ..	29·1	24·6	27·0	28·0	26·2	20·6
13	Double ammonium salts and sulphate of potash..	31·0	28·7	29·7	31·5	33·1	27·4
14	Double ammonium salts and sulphate of magnesia	28·8	22·0	24·1	28·0	24·1	18·9
15	Double ammonium salts, in autumn, and minerals	29·9	26·1	24·1	29·7	29·0	22·3
16	Double nitrate and minerals		30·2	40·4		39·1	42·4
17	Minerals alone, or double ammonium salts alone, in alternate years	14·9*	12·9	13·8	13·0	12·4	11·7
18		29·9†	27·6	27·3	29·5	29·7	24·6
19	Rape cake alone	25·4	22·8	28·6	25·7	24·8	24·7

* Produce by minerals. † Produce by ammonium salts.

On the other hand, Plot 6, dressed with 43 pounds of nitrogen per acre only, is gradually becoming exhausted as far as nitrogen is concerned. The loss is accounted for, apart from the nitrogen removed in the crop, by that removed in the weeds, by drainage, and otherwise.

Plot 10 was manured with nitrogen only, in the form of 400 pounds of ammonium salts, over a long period. It has been established that in spite of the use of nitrogenous manure alone the crop has been well maintained. The nitrogen has produced an average increase of 7·4 bushels, the yield having been fairly steady for the last thirty years. The crop, however, is slow to mature, is liable to rust, and generally presents an unhealthy appearance.

Generally we may say that a cereal crop, such as wheat, may be grown for many years on the same soil without depreciation in productiveness, if sufficient nitrogen, phosphoric acid, and potash is supplied to replace that removed by the crops. It is true that the vigour of the plant does not appear to be so great following a long succession of previous wheat crops as when grown in rotation with other crops, but the yield does not seem to be materially altered.

Continuous corn-growing, however, suffers from the disadvantage that certain weeds tend to accumulate, the difficulty of keeping the land clean being thereby augmented.

As stated above, one of the main objects of the Rothamsted experiments was to test the truth of the opinion advanced by Liebig, that a crop could obtain its nitrogen requirements from the atmosphere alone, if certain mineral constituents were supplied in the form of solid manure.

Plot No. 5, receiving the minerals, but no nitrogen, grows very little more than the continuously unmanured plot. The average over a long period was only 14·9 bushels, as against 13·4 without manure of any kind.

Plots 6, 7, and 8, which have received increasing quantities of ammonium salts, rising from 43 pounds of nitrogen per acre on Plot 6 to double that quantity on Plot 7 and treble the quantity on Plot 8, have yielded crops which increase with each addition of nitrogen. Plot 6 gave 24 bushels, Plot 7, 33 bushels, and Plot 8, 37 bushels. The effect is even more marked on the yield of straw, the figures in each case being 21½ cwt., 33 cwt., and 41 cwt.

With nitrogen alone over a long period of years the crop is considerable, and much superior to that grown by minerals without nitrogen. The plant is deep rooted, and the roots are able to search the soil well for the mineral constituents necessary for the growth of the plant. It is therefore rarely necessary to supply wheat with any but nitrogenous manure. The natural nitrifying processes in wheat are slow during the cool season of the year in which it is grown, and a supply of external nitrogen in the form of manure is therefore all the more necessary.

The increase of crop obtained by the application of nitrogenous manure is not always in direct proportion to the amount of nitrogen supplied. Each addition of nitrogen gives a smaller return in the crop, and this constitutes what is known as the "law of diminishing returns."

TABLE M.—EXPERIMENTS ON WHEAT, BROADBALK FIELD: AVERAGES OVER THIRTEEN YEARS (1852–1864).

		Dressed Grain.		*Straw.*	
Plot.	*Manures per Acre.*	*Produce per Acre.*	*Increase for Each Additional 43 Pounds Nitrogen in Manure.*	*Produce per Acre.*	*Increase for Each Additional 43 Pounds Nitrogen in Manure.*
		Bush.	*Bush.*	*Cwt.*	*Cwt.*
5	Minerals alone	18·3		16·6	–
6	Minerals and 43 pounds nitrogen as ammonium salts	28·6	10·3	27·1	10·5
7	Minerals and 86 pounds nitrogen as ammonium salts	37·1	8·5	38·1	11·0
8	Minerals and 129 pounds nitrogen as ammonium salts	39·0	1·9	42·7	4·6
16	Minerals and 172 pounds nitrogen as ammonium salts	39·5	0·5	46·6	3·9

Table M (p. 141) will illustrate this law, showing the diminishing yield with successive increments of nitrogen applied as manure. It will thus be evident that a point will at last be reached in the manuring of a crop where the increased profit from the acreage under cultivation will not compensate for the increased expenses in connection with the manure and labour. This point, of course, must be carefully judged in relation to the market prices prevailing at the time.

Table N shows the average increase which may be expected from the application of 1 cwt. of sulphate of ammonia as manure.

TABLE N.—INCREASE DUE TO ONE CWT. OF SULPHATE OF AMMONIA, COSTING SEVENTEEN SHILLINGS.

		£	s.	d.	£	s.	d.
Wheat ..	.. 4 bush. at 55s. per qr. 504 lbs.	1	7	6	1	17	6
Wheat straw	.. 5 cwt. at 40s. per ton	0	10	0			
Barley ..	.. 6 bush. at 50s. per qr. 448 lbs.	1	17	6	2	6	6
Barley straw	.. 6 cwt. at 30s. per ton	0	9	0			
Oats ..	.. 7 bush. at 30s. per qr. 336 lbs.	1	6	3	2	0	3
Oat straw ..	.. 7 cwt. at 40s. per ton	0	14	0			
Rye grass hay	.. 10 cwt. at 100s. per ton		—		2	10	0
Meadow hay	.. 8 cwt. at 90s. per ton		—		1	16	0
Mangolds ..	.. 32 cwt. at 12s. 6d. per ton		—		1	0	0
Potatoes ..	.. 20 cwt. at 60s. per ton		—		3	0	0

(Collins, "Plant Products and Chemical Fertilisers.")

Under these conditions the agriculturist could afford to pay some £14 per ton for sulphate of ammonia.

Further experiments were conducted at Rothamsted to test the effect of replacing ammonium salts by nitrate of soda, equivalent quantities being used as far as nitrogen was concerned.

From a consideration of the results from Plots 9 and 16, it will be seen that for wheat nitrate of soda is a more effective source of nitrogen than ammonium salts, the increase in yield amounting to 16 per cent. more grain and 26 per cent. more straw for a single application, a double application, however, yielding practically the same amount of grain and only about 1 cwt. more straw.

Nitrate of soda possesses the property of remaining soluble, diffusing deep into the soil, and encouraging greater range of roots.

Ammonium salts, on the other hand, are retained near the surface, and produce injurious effects, due to the removal of calcium carbonate from the soil, which thus tends to become acid.

After a wet autumn and winter a top dressing of nitrate of soda, 1 to 1½ cwt. per acre, will be found of particular value. The manure to be ploughed in before seeding, when wheat is grown two or three times in succession, should consist of about 1 cwt. per acre of some slow-acting nitrogenous manure and 2 cwt. of superphosphate.

The time of application of ammonium salts as manure is of importance. In the experiments under discussion, as a rule, 100 pounds of the ammonium salts were applied in the autumn, when the seed was sown, the rest being reserved for a top dressing in the spring.

On Plot 15, however, the total quantity of manure – namely, 400 pounds of ammonium salts – was applied in the autumn; otherwise the manuring was identical with that of Plot 7. The crop on Plot 15, however, is on the average below that of Plot 7, showing that some loss has taken place.

This loss does not occur through the direct washing-out of the salts, as they are held very near the surface by the soil itself. Ammonium salts, however, are very readily converted to nitrates in warm, moist ground, especially when the latter has been recently stirred. These nitrates are themselves in turn very readily washed out by heavy rain.

Table O (p. 144) shows that the diminution in yield due to autumn manuring is very dependent upon the rainfall in the ensuing winter.

It would, moreover, appear that the utility of sulphate of ammonia as applied to wheat is confined to the season of its application. Dressings of this salt and minerals applied in alternate years showed that the plot which in any year was receiving minerals without nitrogen derived little or no benefits from the ammonia it had received the year before. On the other hand, the effect of the minerals appears to be carried forward from year to year, and they have effect in seasons beyond the year of their application, as the yield in years when ammonium salts were applied was very little less than that obtained from a normal manure containing both nitrogen and mineral constituents.

TABLE O.—COMPARISON OF SPRING AND AUTUMN DRESSINGS OF AMMONIUM SALTS (WET AND DRY SEASONS RESPECTIVELY).

	Rainfall of Preceding Autumn and Winter (October to March).	*Total Produce, Pounds per Acre.*				*Grain, Bushels per Acre.*			
		Ammonium Salts applied.		*Difference in Favour of Spring Dressing.*		*Ammonium Salts applied.*		*Difference in Favour of Spring Dressing.*	
		In Previous Autumn, Plot 15.	*In Spring, Plot 7.*	*Per Acre.*	*Per Cent.*	*In Previous Autumn, Plot 15.*	*In Spring, Plot 7.*	*Per Acre.*	*Per Cent.*
Mean of eleven years of low winter rainfall*	11·73	5631	5829	+ 196	+ 3·4	31·8	32·5	+ 0·7	+ 2·2
Mean of eleven years of high winter rainfall†	16·73	4932	6004	+ 1072	+ 21·7	27·5	32·5	+ 5·0	+ 18·1
Mean for whole period of sixty years (1852-1911) . .	13·9	5305	5843	+ 538	+ 10·1	30·5	32·7	+ 2·2	+ 7·2

* The years of low winter rainfall were 1889, 1890, 1891, 1893, 1898, 1901, 1902, 1903, 1905, 1906, 1909.
† The years of high winter rainfall were 1892, 1894, 1895, 1896, 1897, 1899, 1900, 1907, 1908, 1910, 1911.

It is well known that sulphate of ammonia exhausts the soil of its lime. This is brought about by the combination of the acid portion of the salt with the calcium carbonate present in the soil, and in certain plots of barley long-continued application of ammonium sulphate will result in the ground becoming practically unproductive.

This soil, however, can be very easily revivified by subsequent dressing with lime to replace that which has been exhausted by means of the sulphate. This point should not be lost sight of when considering the amount of sulphate of ammonia to be applied as fertiliser. Without the lime, sulphate of ammonia will not undergo those nitrifying changes which are necessary for its full usefulness to be developed.

The dangerous period for a wheat crop is either just at the beginning or just at the end of the winter, and in order that these periods should be successfully surmounted top dressings of about ½ cwt. of sulphate of ammonia can very advantageously be used at one time, a subsequent ½ cwt. being added later on if necessary. The second dressing should be given if the plant appears yellow or sickly.

A top dressing is also of use in a period of drought when a crop is only half-grown. Even distribution of such dressings can be obtained by mixing the manure with a small quantity of earth or ashes, the mixture being then distributed broadcast.

Nitrification of the ammonia portion of ammonium sulphate proceeds very slowly in winter, but three weeks of very good weather will nitrify all the ammonia added to the soil. On general grounds sulphate of ammonia should be regarded as a manure to be utilised just before it is needed.

Large leaf development may be expected as a general rule from the use of ammonium sulphate. It is therefore in extensive use among market gardeners and intensive cultivators generally for the production of greenstuff. It is not very suitable for fruit-growing in general, though gooseberries appear to derive some benefit from its application.

Commercial sulphate of ammonia is a very finely crystallised substance, which shows a tendency to stick together, owing to the presence of a few units per cent. of water and a few tenths of 1 per cent. of free sulphuric acid. Recent developments in the manufacture have aimed at producing a white neutral salt equal in quality to the very high grade synthetic product (see p. 157).

In contact with an alkali or strong base the ammonia is liberated, and diffuses into the atmosphere. The salt, therefore, should never be mixed with lime, wood ashes, or basic slag. There are few soils, however, in which the clay and humus do not greatly preponderate over the lime, so that the former substances are able to fix the ammonia in such a manner that loss due to the presence of lime is more or less obviated.

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THE NITROGEN INDUSTRY

PART I

NITROGEN PRODUCTS AND CHILE NITRATE

The Atmosphere.

The existence of an invisible medium—the atmosphere—must have been recognised comparatively late in the history of the world. The Greek philosopher Aristotle (384–322 B.C.), born at Stagira in Macedonia, the greatest thinker of antiquity and the leader of thought for centuries, is said to have made an experiment to test the material nature of the air. He weighed an empty bladder, then blew up the bladder and weighed it again. There was no increase in weight, and it was concluded that air had no weight and was immaterial. The fallacy of this experiment—if it was ever made—was demonstrated by the work of Archimedes (287–212 B.C.), born at Syracuse, and described as the greatest inventive genius of antiquity. In his celebrated principle of hydrostatics, Archimedes demonstrated that a body weighed in water loses weight equal to the weight of the water which it displaces, and the same relation holds for a body weighed in air. The air filling the bladder in Aristotle's experiment would displace its own volume of the external air, the weight of which would exactly counterpoise that of the air inside the bladder. The first demonstration of the material nature of the air is due to Otto von Guericke, Burgomaster of Magdeburg, the inventor of the air-pump. Guericke in 1650 weighed a glass globe, fitted with a stopcock, which he had exhausted of air by the air-pump. On opening the stopcock, air rushed into the globe and the latter became heavier. Exact experiments have shown that the density of the air is 76·5 pounds per 1,000 cubic feet at 15° C. and

1 atmosphere pressure. Since 1 cubic foot of water weighs 62·5 pounds, it follows that water is rather l[illegible] than 1,000 times heavier than air.

The chemical composition of the air was clearly elucidated only at the end of the eighteenth century, by the famous French scientist Lavoisier (born 1743; guillotined 1794). Since the commonest chemical change is the combustion of substances in air, it might have been expected that the chemical nature of the latter, which is comparatively simple, would have been discovered at a much earlier date. As a matter of fact the English chemists Robert Boyle (1627–1691), Robert Hooke (1635–1703), and John Mayow (1645–1679) came very near to the elucidation of the composition of the air and the nature of combustion. Boyle made a great number of experiments on the air, both physical (leading to the discovery of "Boyle's Law" in 1662, that the pressure of a gas is inversely proportional to its volume) and chemical. In the latter he found that substances will not burn in a receiver exhausted by an air-pump, so that the air is necessary for combustion. Boyle found, however, that gunpowder will burn in the entire absence of air, so that he was puzzled and not quite sure whether air was necessary for combustion or not. His assistant Hooke (the inventor of the spring balance wheel of watches, and the first Secretary of the Royal Society) went farther. He found that charcoal and sulphur burn with great brilliance when thrown into fused nitre or saltpetre, and thence supposed that there is something common to air and nitre, which supports combustion. This he called "nitre air." The gunpowder in Boyle's experiment contained nitre, and could therefore burn in the absence of air. Hooke's experiments were greatly improved and extended by Mayow, who proved in addition that nitre air is absorbed in the respiration of animals. Neither Hooke nor Mayow was able to isolate nitre air.

These beginnings of a true theory of combustion were soon stifled by an erroneous dogma, due to two German chemists, which persisted for half a century and obscured every branch of chemistry. This was the famous theory of phlogiston of Becher and Stahl.

Johann Joachim Becher (1635–1682), who led a wandering life and was more apt at theorising than experimenting, supposed that combustibles contain a " fatty earth " which is the principle of combustibility. Becher's idea would probably have passed into oblivion had it not been revived and explained at great length by his countryman, George Ernst Stahl (1660-1734), Professor of Medicine at Halle and later physician to the King of Prussia, who popularised the doctrine in an improved form in his lectures. Stahl gave to Becher's principle the name "phlogiston," from a Greek word meaning "flame," and supposed that combustible bodies are rich in phlogiston. When combustion takes place, phlogiston escapes. The phlogiston may be restored to a burnt material, such as calcined lead, by heating with another material rich in phlogiston, such as charcoal.

The theory of phlogiston was so simple and plausible that its accuracy might have been suspected *a priori*. It entirely failed to explain why, although phlogiston escaped, a body after combustion weighed more than before. Nevertheless, the theory was accepted by practically every chemist, and formed the basis of most of the chemical textbooks of the eighteenth century. It was overthrown by the experiments of Lavoisier, who showed that the gain in weight in bodies on combustion was due to the absorption of part of the air—namely, the " nitre air " of Hooke, which had previously been isolated from nitre by the Swedish chemist Scheele in 1772. This part of the air was called Oxygen (Greek, "acid producer ") by Lavoisier, since many substances form acids when they burn; the other part of the air, which does not support combustion or life, he called Azote. The latter is now usually called Nitrogen, since it is one of the elements of nitre. The air consists principally of a mixture of the two gases, oxygen and nitrogen. Oxygen was independently discovered by Joseph Priestley in 1774.

Henry Cavendish (1731-1810), the English chemist, found in 1784 that the nitrogen of the air probably contains about 1 per cent. of another gas, which, unlike nitrogen, does not combine with oxygen. This gas was discovered by Sir William Ramsay and Lord Rayleigh in 1895, and called Argon.

The Composition of Air.

Atmospheric air consists principally of the two gases nitrogen and oxygen mixed together in the proportions of roughly 4 to 1 by volume respectively. Small amounts, a little under 1 per cent. by volume, of the so-called Inert Gases—argon, helium, neon, krypton, and xenon—are also invariable constituents of air, and moisture and carbon dioxide are always present in varying amounts. The exact composition of air, free from moisture, carbon dioxide, and other impurities, according to Leduc, is as follows:

	Per Cent. by Weight.	*Per Cent. by Volume.*
Nitrogen	75·5	78·06
Oxygen	23·2	21·00
Inert gases	1·3	0·94

The percentage of oxygen in air is not quite constant, as was formerly supposed; it varies to the extent of about 0·1 per cent., according to the locality and altitude. The amount of carbon dioxide present in air is usually about 3 volumes in 10,000 of air; it rises to two or three times this amount in towns during fogs, and in badly ventilated localities the percentage may rise to ten times the normal amount.

A table giving the composition of the air more completely is the following:

	Per Cent. by Volume.
Nitrogen	78·05
Oxygen	21·0
Argon	0·932
Neon	0·00181
Helium	0·00054
Krypton	0·0000049
Xenon	0·00000059
Carbon dioxide	0·03 to 0·3
Hydrogen	0·003
*Methane	0·0121
*Other hydrocarbons	0·002
Formaldehyde	0·002 to 0·005

Ozone, Hydrogen Peroxide, Ammonia, Nitric Acid and Oxides of Nitrogen, Sulphur compounds (especially Sulphuric Acid

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* Doubtful; amounts probably very variable.

near towns where coal is burnt), Chlorine compounds (including common salt carried inland from the spray of the sea), water vapour, soot, bacteria, traces of radium emanation, etc., are also present in varying and usually small amounts. The atmosphere is, therefore, as Boyle expressed it ("Works," vol. ii., p. 345, London, 1700), "an Aggregate of various kinds of *Effluvia* jumbled and mix'd together."

The inactive gases—argon, etc.—are peculiar in that they form no compounds with other elements and are always found in the free state. Some of them—*e.g.*, xenon—occur in exceedingly small amounts: as Ramsay, their discoverer, said, "There is more gold in sea water than xenon in the atmosphere." The gases argon, neon, and helium are now used commercially. Argon is extracted from the air and used for filling the best types of metal-filament electric lamps. The vacuous lamps are rapidly blackened by the volatilisation of the metal (tungsten) filament by the heat generated by the current; if the lamp is filled with argon to about one-third of an atmosphere pressure, the blackening is much reduced. Argon is now made by the British Oxygen Company at Wembley for this purpose. It is also made in America, Germany, and France. Argon is extracted from the air by the Claude process at Boulogne; 93 per cent. argon is sold at 1s. 3d. per litre, 87 per cent. argon at 1s. American gas (from the Linde process) is said to contain only 40 per cent. of argon.

Neon is extracted from the air and used under low pressure in the electrodeless Moore lamps, which glow with a beautiful red light. Such a lamp was installed in the courtyard of the Savoy Hotel; they have been used for advertising purposes. Helium is not extracted from the atmosphere, but from the gases of certain natural-gas wells in the U.S. at Kansas, and in Canada at Medicine Hat. These gases contain about 1 per cent. of helium, which is extracted by a complicated process, and has been used, alone or mixed with hydrogen, for filling airships, since it is a light gas (although it is twice as dense as hydrogen) and is not inflammable. Previous to the late war the Germans were experimenting with helium for filling Zeppelins, but the source of the gas was too limited. In England, early in the war, Sir William Ramsay suggested the ıse of helium for airships, and got into communication with Americans who were interested in the matter. The latter kept back the information in their possession, but the whole matter was investigated *a priori* in a masterly fashion by Professor McLennan, of Toronto, who showed how the helium of Canadian gas could be extracted, measured its properties, and carried out investigations on its use, mixed with hydrogen, in balloons and airships. Professor McLennan's work is summarised in his lecture to the London Chemical Society, published in their journal of July, 1920. More recently it has been asserted that the cost of helium for filling an airship would exceed the cost of the ship. In view of the recent disaster to the airship R38, however, it would seem that the matter is still worthy of careful consideration.

Separation of Nitrogen and Oxygen Gases from the Air.

Since nitrogen and oxygen are simply mixed together in the atmosphere, and are not bound together in chemical combination, as are hydrogen and oxygen in water, their separation may be carried out by purely physical methods—*i.e.*, methods not involving the use of chemical reagents nor the expenditure of large amounts of energy. It is known that in separating the constituents of a mixture of gases a certain small amount of energy must be expended, in opposition to the general tendency of gases to diffuse into one another and mix uniformly, but this is very small in comparison with the energy required to split up the compound water into its elements, say by means of an electric current.

Oxygen was formerly manufactured from air by a chemical process devised by Boussingault in 1852, but improved and made into a workable technical method by the brothers Brin in 1879. In this so-called "Brin process" the purified air was passed over baryta (a substance resembling quicklime), heated to dull redness in iron retorts. Baryta is an oxide of barium, BaO. Under the above conditions it picks up more oxygen to form barium peroxide, BaO_2, the nitrogen of the air passing on unabsorbed. If the pressure was now reduced, the barium peroxide decomposed into baryta, which was used over again, and oxygen gas, which was pumped off and compressed into steel cylinders for sale.

The Brin process was in use until about 1902. It has now been replaced by a physical method of separation depending on the fractional distillation of air which has been liquefied by intense cold.

Nitrogen boils at a lower temperature than oxygen, and the first fractions of evaporated liquid air are richer in nitrogen than the later fractions. By making the vapour bubble through the liquid in a fractionating column, as in the three methods of Hampson, Linde, and Claude, nearly pure nitrogen and oxygen are obtained from liquid air. The principle is the same as that adopted in the separation of alcohol from water in the manufacture of spirit by the distillation of fermented liquids. The difference lies in the very low temperatures involved in the separation of the constituents of the air. The boiling-points of oxygen and nitrogen are - 183° C. and - 196° C. respectively. The helium, neon, and argon may also be separated by a slight modification of the apparatus, since their boiling-points differ from those of the other gases, and argon is at present made in this way by the British Oxygen Company for lamp-filling. The manufacture of oxygen by the fractional distillation of liquid air has assumed a position of great importance, and has practically displaced all the older methods, such as the Brin process. The British Oxygen Company has plants capable of turning out one and a half to two million cubic feet of oxygen gas, or about 180 tons, per day. In Germany, according to Sir James Dewar, a single-unit plant is capable of producing nearly as much oxygen in a day as the whole of the British plants.

The three technical processes for the separation of oxygen and nitrogen from the air by the liquid distillation process are those of Hampson (used, with the other processes, by the British Oxygen Company; patented in England in 1895), of Linde (used by the Gesellschaft für Lindes Eismaschinen A.-G. in Germany; patented in 1895), and of Claude (used by the Société de l'Air Liquide; patented in 1902). In broad principle the processes are similar, though they differ in important details.

The first step is the liquefaction of the air. Early experimenters such as Natterer attempted to do this by applying enormous pressures (2,000 atmospheres: 1 atmosphere = 14·7 pounds per square inch), but without success. Progress became possible as a result of some purely academic work of Professor Andrews of Dublin in 1869, who showed that under no circumstances can a gas be liquefied unless it is first cooled below a certain temperature, characteristic of each gas, called its *critical temperature*. It was thought probable that the critical temperatures of oxygen and nitrogen, which are the main constituents of air, are much lower than any which can be attained by the most efficient freezing mixtures. The problem was, therefore, to devise a method of producing intense cold. This, again, had been solved by another purely academic research, carried out to settle a purely theoretical problem in thermodynamics by Lord Kelvin and Dr. Joule in 1852–1862. Kelvin and Joule found that if a stream of compressed air was allowed to escape through a nozzle or valve into the free atmosphere, the gas cooled itself slightly. This slight cooling represented the energy expended in separating the molecules of the gas, when expansion occurred, against the very slight attractive forces operative between them, and is called the Joule-Kelvin effect. In the case of air the Joule-Kelvin effect is such that if air at 0° C. and under 100 atmospheres pressure is allowed to expand to 1 atmosphere pressure, it cools itself to – 24·7° C.

The step from this to the liquefaction of air was not great, and was possible as a result of an invention of the German scientist Siemens, made in 1857, known as the "heat exchanger." Suppose that air cooled by expansion, as described above, is allowed to sweep over the surface of a copper pipe, which is a good conductor of heat, bringing the compressed air, at 0° C., to the expansion nozzle. This air will be cooled by giving up heat to the cold air outside, the latter being warmed nearly to the temperature 0°, so that no loss of cold will result in the escaping air. The compressed air will arrive at the jet cooled much below 0° C., and it will become about 30° C. colder still on expansion. This very cold air will again take heat from the compressed air coming down the pipe, and soon the cooling effect accumulates to such an extent that the air is cooled to the temperature of liquefaction, and a jet of liquid air then escapes from the expansion nozzle.

This liquid air contains the oxygen and nitrogen in proportions different from those in which they occur in the atmosphere—*e.g.*, 50 to 60 per cent. of oxygen. If it is allowed to evaporate, the nitrogen, being more volatile, tends to pass off first, but the separation in this way is very imperfect. The liquid is raised to the top of a tower fitted with perforated shelves, placed inside the coil in which heat-interchange occurs, the whole apparatus being carefully lagged to prevent ingress of heat from outside. Below the tower is a pot in which is a spiral of pipe through which the compressed air, cooled by heat-interchange, passes on its way to the expansion nozzle. This air, being slightly warmer than liquid air, boils the latter in the pot, and the "vapour," richer in nitrogen than the liquid air, bubbles through the liquid air running down the tower from the expansion nozzle. This cold liquid air condenses out practically all the oxygen in the gas rising through it, so that essentially only nitrogen passes out at the top of the tower, and fairly pure liquid oxygen runs out at the bottom. The latter is also evaporated in a similar way, and the two very cold gases are passed through heat-interchangers so that their cold is utilised. The gases are then compressed into steel cylinders at 100 atmospheres pressure for sale.

A detailed account of the methods use for the liquefaction of air and the manufacture of oxygen and nitrogen will be found in Greenwood's "Industrial Gases" (Baillière, Tindall and Cox, 1920, pp. 58–133).

The separation of the atmospheric gases has been carried out to the largest extent in Germany. The pioneer firm is the Gesellschaft für Lindes Eismaschinen A.-G., in Hollriegelskrueth, near Munich. Owing to the stringent blockade of Germany during the war, the demand was much less for oxygen than for nitrogen. The process for the production of these two gases in a pure state is much the same, but in most cases the requirements are not such that both gases must be obtained pure at the same time. Under normal conditions, in plants for the production of pure oxygen (an average of

·98 per cent.), the nitrogen is drawn off with 3 to 4 per cent. oxygen content, whereas during the production of pure nitrogen (99·6 per cent. and above) the oxygen residues will be only of 60 to 80 per cent. purity. It is possible, however, and in some cases it has actually been accomplished in practice, to reclaim a portion of the oxygen residues in a perfectly pure state. Only in rare cases, however, will this be required, because up to the present it has not often been necessary to supply large quantities of oxygen and nitrogen at the same time and in the same place. It will be explained later that such contingency may arise in future.

During the war the most important application of nitrogen in Germany was for the production of calcium nitrate, for which in Germany five installations with a total hourly capacity of about 22,000 cubic metres, and in Austria four plants with a total hourly capacity of 3,500 cubic metres, of nitrogen gas were installed by the Linde Gesellschaft. The largest of these installations is composed of six units, each of an hourly capacity of 1,700 cubic metres, and is situated in the former Government Nitrate Works at Piesteritz, near Wittenberg, on the Elbe. This plant is probably the largest nitrogen-producing plant in the world, and was completed and set to work in 1915 within the short period of ten months. Although this plant was designed in such a manner that only four units were in operation at one time, it was for many months in continuous operation with five units, with an hourly capacity of nearly 9,000 cubic metres. This has only been possible because the separation apparatus worked for over five weeks continuously without having to be shut down or thawed out. With most other apparatus the drawback is that the carbonic acid and moisture of the air freeze up and clog the separating apparatus. With the plant in question these difficulties have not been in evidence. The carbonic acid is separated under pressure by means of caustic soda solution, whereas the water is removed by cooling the air to about - 30°C. by means of a refrigerating machine and special air coolers, which are changed from time to time. The power consumption in these plants amounts roughly to ⅓ h.p. hour per cubic metre of nitrogen. The air compressors employed are four-stage compressors for a maximum pressure of 1,750 pounds per square inch, which, however, is only required during the initial cooling period of the separation apparatus. The final pressure normally employed amounts to 575 pounds per square inch. The machinery equipment was supplied by the Berliner Maschinenbaugesellschaft vorm. Schwartzkopff, and is coupled direct to electric motors by Siemens-Schuckert. An installation of the type described uses three sets for a capacity of 2,000 cubic metres per hour. In this installation 2,000 cubic metres of pure nitrogen (of 99·6 per cent. purity required for the manufacture of calcium nitrate) and 200 cubic metres of oxygen of a degree of purity of 95 per cent. are produced. Three similar installations with a total output of 10,000 cubic metres per hour are in the course of erection for the production of synthetic ammonia by the Haber process. These intallations are intended for the two large works of the Badische Anilin und Sodafabrik in Oppau and Merseburg.

In this latter plant (see p. 165) three units, of an hourly capacity of 2,500 cubic metres each of pure nitrogen, and 200 cubic metres of oxygen, are installed. The power consumption in these installations is roughly ¼ h.p. hour per cubic metre of nitrogen.

Numerous oxygen-producing plants have been erected for various purposes. The employment of oxygen for autogenous metal welding has become indispensable to the entire metal industry, and in Germany about 14 million cubic metres of oxygen were said to have been used for this purpose in 1920. This quantity of oxygen is supplied by larger or smaller plants distributed over the whole of Germany, and partly also by large consumers on their own premises. The plants supplied by the Linde Company consume roughly 1·6 to 2 h.p. hours per cubic metre of oxygen, measured under atmospheric pressure, and supplied, for a pressure of 2,200 pounds per square inch, in steel cylinders. The power consumption decreases as the size of the plant increases.

In some works a certain quantity of pure nitrogen is produced besides the oxygen, which is likewise compressed into steel cylinders.

Argon is obtained with some little difficulty, on account of the closeness of its boiling-point to that of oxygen. The Linde Company also state that they have supplied two installations for oxygen, one with three units each of 300 cubic metres and the other of three units each of 600 cubic metres per hour, for the new arc process (see p. 253). In these installations the power consumption amounts to 0·9 to 1 h.p. hour per cubic metre of oxygen. These are stated to be among the largest oxygen plants in the world.

Details of oxygen and nitrogen plants in other countries than Germany are not readily available, but it is known that the unit capacity is much less at the present time. Some of the largest plants outside Germany are working in connection with nitrogen-fixation processes in Norway and America. At Odda (Norway) a Linde plant, actuated by a 200 h.p. motor, is capable of producing 100,000 cubic feet of nitrogen per hour. It consists of seven units, the three older units having a capacity of 13,000 cubic feet, and the four new units producing 24,700 cubic feet. The nitrogen contains less than 0·4 per cent. of oxygen. In the new Alby works (Norway) a Claude apparatus is installed, the nitrogen from which contains even less oxygen. Very large Claude plants are installed in the U.S. Government Nitrate Factory at Muscle Shoals, Alabama, Ga., an account of which will be found in the section of this book devoted to cyanamide (p. 188).

The preparation of nitrogen gas is a technical process which has already been highly perfected, and very little improvement is to be expected in this direction. Recent costly experiments in America, with a view to improving the apparatus, have led, apparently, to no very decisive results.

The cost of the production of nitrogen from the air, by liquefaction and fractionation, was estimated before the war at about 6d. per 1,000 cubic feet of the gas.

If the value of the oxygen is taken into consideration this price would be reduced. The cost of oxygen made by this process was about 10d. to 1s. per 1,000 cubic feet, pre-war, although the selling price was in the region of £4 per 1,000 cubic feet to large users. In some cases the patentees of plants made the stipulation that oxygen plants were not to be used for the production of nitrogen, and *vice versa*, since the firms supplied both oxygen and nitrogen plants. With the recent improvements of plant, in which the same machine is capable of supplying either oxygen or nitrogen in a nearly pure condition, and the remaining gas reasonably pure, this restriction is hardly likely to survive. It is only by its promoters keeping fully abreast of all scientific progress throughout the world, and by preserving an elasticity capable of responding to changing conditions and varying markets, that an industrial enterprise can hope to hold its own.

The Nitrogen Products Committee appointed by the Minister of Munitions during the war states* that the oxygen and liquid air industries in this country cannot be said to have enjoyed a free and unrestricted development on a competitive basis, that the prices hitherto prevailing for the compressed and liquid products have not been conducive to their employment to the fullest extent in the important directions mentioned, and have served to debar their use in other industries in which cheap and, perhaps, low-grade oxygen might have been utilised with advantage. They recommend that "all liquid air nitrogen plants used in connection with nitrogen-fixation installation in the United Kingdom should be operated to the maximum advantage for supplying the growing home demand for oxygen and argon," and that "the imposition of restrictive trade agreements—such as have been operative at nitrogen-fixation installations abroad—which prevent the recovery and utilisation of by-product oxygen from nitrogen plants, should not be permitted in this country." Mr. K. S. Murray, of the British Oxygen Company, has (*J. S. C. I.*, 1920, 54R) criticised some of these conclusions somewhat severely, and dealt with some important points in detail. The main question of cost is, however, not satisfactorily met.

In some quarters the ideal of British manufacturers appears to be some form of "protection" and complete elimination of competition between themselves and more progressive foreign competitors. Parliament has been pressed to carry out some "pledge" which is understood to have been given, and has passed, and is being urged to pass further, legislation which will have the effect of giving certain firms and combines an unwholesome monopoly in production and marketing. This policy will lead to nothing but disaster. The British markets alone cannot sufficiently recompense undertakings of any magnitude, and in the fierce struggle for the markets of the world the artificial protection of incompetence will prove a broken reed. This truth seems already to be making itself felt in more than one quarter.

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* Final Report of Nitrogen Products Committee, H.M. Stationery Office, London, 1920. Price 4s.

The *Observer* of October 31, 1920, said: "Too many employers and too many employed have imagined, if they thought about it at all, that they were living in an industrial golden age. It is now coming to a cheerless end. Prices which ruled in a famine period are now restricting demand. We have produced, and are producing, much below our capacity; there is no plenty, and there is no cheapness. Meanwhile, the other factor in our recovery, the absence of our most formidable competitor from the markets, is not permanent. Germany, with such resources as she has, is working. Nothing can prevent a nation of sixty millions, skilful, industrious, and well equipped, from taking again her place in the world as a producer. Puny and pretentious attempts to defer that day by political devices will be swept aside by natural forces."

"The trade and commerce of the world, in spite of idealists, will gravitate to the groups of men in any country who are able to produce cheaper and better than others" (Lord Leverhulme).

The Properties of Nitrogen.

Although it is not a completely inert element like argon, nitrogen shows little tendency to enter into combination with other elements. In this respect it differs remarkably from oxygen, the second main constituent of air, which is characterised by the readiness with which it unites with other substances. The oxidation of carbon, which is the principal change taking place in the combustion of coal, is the source of practically the whole of the energy utilised in Great Britain—and, in fact, in most countries except those having water-power. Even in countries utilising water-power a considerable proportion of the useful energy is obtained by the combustion of coal.

Nitrogen is a gas without taste or odour, and but sparingly soluble in water. It does not support combustion or life, and combines directly with very few elements; with these union occurs only with difficulty and at high temperatures. Two compounds of nitrogen which can be formed directly are of great importance.

Compounds of Nitrogen.

The compound of hydrogen and nitrogen is Ammonia, NH_3, which is a gas produced to a limited extent when electric sparks are passed through a mixture of nitrogen and hydrogen. Ammonia itself is decomposed by electric sparks into its constituent elements, so that when the compound is formed from its elements by the passage of electric sparks, it is at the same time decomposed. When a certain percentage of ammonia is present, as much is formed per second as is decomposed, and a state of equilibrium is set up; any further passage of sparks leaves the composition of the gaseous mixture unaltered. It would then be a waste of time and electric energy to attempt to obtain any more ammonia by continuing the passage of electric sparks. By shaking the gas with water, the ammonia is dissolved, forming the familiar solution known as "ammonia," and the residual gas may again be treated as described for the production of a further quantity of ammonia.

When, instead of a mixture of hydrogen and nitrogen, a mixture of oxygen and nitrogen is taken, and electric sparks passed through it, combination also occurs slowly and an oxide of nitrogen is formed. This is Nitric Oxide, NO. The reaction is also reversible, and a state of equilibrium is reached after a time, when no further combination occurs on prolonging the sparking.

The two chemical changes described above are represented as follows:

I. Nitrogen + Hydrogen = Ammonia

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

II. Nitrogen + Oxygen = Nitric Oxide

$$N_2 + O_2 \rightleftarrows 2NO$$

The arrows show that the reaction may take place in both directions—*i.e.*, it is a reversible reaction. A state of equilibrium is attained by reason of the reversibility of the reaction.

Although ammonia does not change when mixed with oxygen, nitric oxide absorbs a further quantity of oxygen to form red vapours of nitrogen dioxide, NO_2, which contains, for the same weight of nitrogen, twice as much oxygen as nitric oxide:

$$NO + O = NO_2$$

Nitrogen dioxide is not formed directly on sparking nitrogen and excess of oxygen together, since it is decomposed by heat into nitric oxide and oxygen, and cannot exist at the temperature of the spark. On cooling, however, nitrogen dioxide is formed, and the gas becomes faintly yellow from the small amount of nitrogen dioxide contained in it. If now this gas is brought in contact with water, in presence of excess of oxygen, the nitrogen dioxide dissolves and a solution of Nitric Acid ("aqua fortis") is formed:

$$\text{Nitrogen dioxide} + \text{Oxygen} + \text{Water} = \text{Nitric Acid}$$
$$2NO_2 + O + H_2O = 2HNO_3$$

Ammonia is an alkaline substance, whilst nitric acid is a powerful acid. The uninteresting properties of the element nitrogen itself give no clue to the protean modifications exhibited by nitrogen in combination with other elements; compounds of nitrogen show an astonishing diversity of properties. Who could predict that the material of beefsteak consists of the same elements, carbon, hydrogen, oxygen, and nitrogen, as the powerful explosive trinitrotoluol, or that the comparatively mild drug quinine should also consist of the same elements as the powerful poison strychnine? From a few building-stones in the form of chemical elements, Nature or the skill of the chemist raises the most varied structures, applicable to widely different needs of life. In the study of the compounds of nitrogen the immense possibilities of synthetic chemistry are seen with most compelling force.

The possibilities of modern chemistry have revolutionised business methods. The scientific chemist knows that, by means of his research, a commercial process on which thousands of pounds have been expended may at any moment become obsolete. No amount of purely business skill is of the slightest avail when this occurs. Natural sources of material, for the acquisition of which much has been spent in money and often in lives, may be rendered useless by some discovery quietly made in the laboratory. The indigo plantations of India were superseded by artificial indigo. The scientific chemist, by whose labours these changes are brought about, is quite well aware of his position, although the noisy and self-important politician makes a much greater appeal to the community at large. Those nations may be expected to make the greatest progress which are best able to utilise the fruits of scientific discovery. Chicanery in business and politics may give a temporary advantage, but the sifting process is none the less sure, although it is slow. Even when political shiftiness is combined with intelligence, as it was in Imperial Germany, its end is still assured. When intelligence is lacking, the process of disintegration may be rapid.

Combined nitrogen is a constituent of some of the most important chemical compounds in nature and industry. In addition to ammonia and nitric acid, which are used in combination with acids and bases, respectively, as plant fertilisers, nitrogen enters into the composition of all vegetable and animal tissues, in the form of Proteins, which are complicated organic substances containing carbon, hydrogen, oxygen, and nitrogen, and sometimes sulphur and phosphorus. The average nitrogen content of proteins is 16 per cent. Combined nitrogen is also a constituent of explosives, such as gunpowder, gun-cotton, cordite, nitroglycerin, dynamite, blasting powder, T.N.T., and picric acid. It enters into the constitution of numerous dyes, such as indigo and aniline dyes, and of drugs, such as quinine, strychnine, morphine, antipyrine, and cocaine. Fertilisers, foods, dyes, drugs, and explosives—the fields of application of combined nitrogen are almost coextensive with civilisation itself.

Fixation of Nitrogen.

In the free state, as it is presented to us in enormous quantities in the air, nitrogen is quite inert. The air over a square mile of the surface of the earth contains 20,000,000 tons of nitrogen awaiting utilisation. The natural sources of combined nitrogen are few, and are rapidly approaching exhaustion. The nitre-fields of Chile at present supply a large part of the world's consumption of combined nitrogen. The rest is furnished, apart from new processes, by the ammonia obtained from coal in the manufacture of coal gas, and of metallurgical coke in coke ovens. Coal contains about 1 per cent. of combined nitrogen, and a small part of this, about one-fifth, comes over with the gas and tar when the coal is destructively distilled in gas and coke making, and is recovered in the form of ammonia. The ammonia is neutralised with sulphuric acid, and the ammonium sulphate is used chiefly as a fertiliser. Chile nitre, which is sodium nitrate, $NaNO_3$, is also largely used for the same purpose. Plants take up combined nitrogen from the soil, and unless this is replaced the soil gradually becomes sterile. The fertile soils of the United States are becoming progressively impoverished, and the area of cultivation is moving slowly further and further west.

The annual output of nitre from Chile is about one million tons, and the deposits are slowly becoming exhausted. The nitrogen present in the air above one square mile of the surface of the earth is thirty times that contained in the combined annual outputs of Chile nitre and by-product ammonium sulphate. Varying estimates of the possible life of the Chilean nitre-beds have been given. The most reliable put this at from one to three hundred years. When the nitre-beds are worked out, and no other sources of combined nitrogen become available in the meantime, the outlook, as the late Sir William Crookes pointed out, is simply starvation for the human race.

The Nitrogen Problem is this problem of avoiding the ultimate starvation which awaits us unless some other source of combined nitrogen is found, and the question of the solution of the nitrogen problem is one in comparison with which the political bickerings, known as "statesmanship," shrink into the minutest insignificance. The problem can be solved only by experimental research, and as the pinch becomes increasingly tighter the true relative importance of science and politics may be expected to become more and more apparent

For various reasons all civilised countries, except Great Britain, have already taken active steps in the way of the solution of the nitrogen problem. Those who were in a position to know the facts during the late war realised that the sea transport of nitre, which was used in prodigious amounts for the manufacture of explosives, was exposed to great dangers of submarine attack, and that ships that should have been carrying food were laden with nitre from Chile. The position at one critical period, as the authors are well aware, was of the gravest character: the stock of nitrates was to be reckoned in weeks, not months. Still another claim for winning the war might be advanced on behalf of Chile; at any rate, it is quite certain that without Chile the Allies would speedily have been reduced to impotence. The possibility that such a state of affairs might come to pass was not unknown to some naval officers, and the warning of Sir Percy Scott is probably remembered. The political heads of the country, however, seem to have had at the beginning no inkling of the real situation, nor of the proper way to meet it. At the very time when fixed nitrogen in the form of Chile nitre was being imported into the country at great risk and expense, no less than 60 per cent. in 1915, and 70 per cent. in 1916, of our own source of combined nitrogen—ammonia—was being exported! Not only was this drain permitted, but large quantities of sulphuric acid, urgently needed for the manufacture of munitions, were used for the production of this exported ammonium sulphate. At a time when every effort was being made to increase the output of sulphuric acid for munitions, 294,000 tons of chamber acid in 1915, and a minimum of 259,000 tons in 1916, were actually sent out of the country in the form of ammonium sulphate! Those in authority were probably not aware that sulphuric acid was used in the manufacture of this product. We surely won the war in spite of "statesmanship." It was at a comparatively late stage of the war, when the menace of starvation was by no means imaginary, that fixed nitrogen was dimly recognised as in some way necessary to war, and feverish preparations were made for the erection of synthetic nitrate factories. These were obstructed at every turn. The immense German Haber factory at Merseburg was erected and working in a little short of a year, but there is still no British works of any kind for the fixation of nitrogen. The Armistice put a stop to the very modest progress which had been made in two years—amounting to the purchase of some material and the erection of a few sheds, on a site convenient for Zeppelin attack, and the "National Factory" is now owned by private interests. Progress under the new conditions does not seem to have been any more remarkable than previously.

The producers of ammonium sulphate have, within the last few months realised that a synthetic ammonia process is in being in Germany, and from recent announcements it may be inferred that the producers of Chilean nitre are also becoming uncomfortably aware that the synthetic processes in other countries are likely to become a menace before very long. The ostrich is about to lift its head from the sand. It is to be feared that a disconcerting spectacle will await its clouded vision. "Protection" will doubtless be the remedy once more.

The position in this country during the war was in sharp contrast to that of Germany. Before the war Germany was the world's largest producer of sulphate of ammonia and the world's largest consumer of Chilean nitrate. In 1913 Germany consumed 480,000 tons of sulphate alone out of a production of 521,000 tons, 20,000 tons only of which was synthetically produced, and 750,000 tons of Chilean nitrate. The total German production of nitrogen products in 1913 represented 110,000 metric tons of nitrogen. It is estimated that in 1917 her total requirements represented 415,000 metric tons of nitrogen, showing a deficiency of 305,000 metric tons, and the cessation of imports rendered it essential to make up the deficit as far as possible by augmenting home production.

In addition to increasing the output of her by-product ammonia industry from 413,000 metric tons of ammonium sulphate in 1914 to an estimated total of 700,000 metric tons in 1917, Germany resorted for the manufacture of the essential nitrogen compounds to synthetic processes on the perfection of which she has spent millions of money. By means of the Haber process and the oxidation process, untried in this country before the war, Germany rendered herself secure, so far as munitions went, until her chemical factories were bombed by the Allies.

It is estimated that the actual production by the synthetic ammonia process in Germany was extended from 60,000 tons of sulphate of ammonia in 1914 to 500,000 tons in 1917, which has since approached 1,000,000 tons, and that the ammonia oxidation process, though only capable of producing nitric acid at the rate of 120,000 tons per annum in 1916, was expanded to meet the military requirements of the Central Powers, which were estimated to be 450,000 tons in 1917. The cyanamide industry was also expanded to such an extent that, although only having an output of 24,000 tons of cyanamide in 1913, it had an estimated minimum productive capacity of 500,000 tons in 1917. By the use of these processes Germany is estimated to have produced in 1917 nitrogen products equivalent to 320,000 metric tons of nitrogen, thus more than wiping out the deficit. It is probable, according to the Nitrogen Products Committee, that these figures are not altogether complete, as processes other than those mentioned are believed to have yielded substantial results. Germany's success, indeed, lends colour to the theory that she did not declare war until she saw her way clear to produce within her own borders by synthetic processes all the nitrogen products required for the great scheme of world conquest.

The Nitrogen Products Committee state that the existing sources of supply of combined nitrogen in the United Kingdom proved wholly inadequate for meeting the war demands, and that they must be considerably increased if the present and prospective home demands are to be met and the pre-war scale of exportation maintained. They also point out that the nitrogen-fixation industries developed in Germany during the war represent post-war assets of considerable value, and it is probable that they will not only enable that country to meet increasing requirements for ammonia and cyanamide nitrogen for some years to come, but will place her in a strong position for competing in the nitrogen markets of other countries.

In a section discussing the influence of the war on future policy the Committee state that if a country is to rely on Chile nitrate for meeting a war demand of the magnitude necessitated by the conditions of modern warfare, that country must be prepared (assuming, of course, that Chile is not a belligerent) to face a heavy demand on shipping, a large advance in the price of imported materials, and a consequent increase in the cost of products manufactured from them.

Reliance upon synthetic methods for a war demand would mean that a country must be prepared to face a large initial capital outlay, but, as compared with the Chilean nitrate process, "two years' expenditure upon imported raw material would alone more than cover the estimated pre-war capital outlay for synthetic installations capable of furnishing the same amount."

Since fixation processes are thoroughly reliable even when installed as emergency measures under war conditions, as experience in Germany showed, and since very serious risks are involved in relying upon overseas shipments of raw material, the Committee say: "The conclusion seems evident that considerations of national safety, of finance, and of utility would force a country to resort to a policy of adopting synthetic methods as an insurance against future emergencies instead of placing reliance upon the importation of Chilean nitrate. . . . Assuming the employment of steamers each capable of carrying about 5,000 tons dead weight and making three round voyages per annum between Chile and Europe, the requirements for nitrate alone would necessitate the constant service of a fleet of about forty-eight steamers."

Another important factor in deciding the relative merits of natural or by-product and of synthetic nitrogen products is that of quality. Prior to the outbreak of the late war, according to a recent article, "the British producer of sulphate of ammonia gave no heed whatever to the chemical and physical characteristics of his product. He knew that, although the home consumer was a comparatively negligible quantity, the export market invariably absorbed the balance; and—beyond the test for nitrogen content—practically no questions were asked as to other chemical properties or general appearance. The middleman or shipper was largely responsible for this state of apathy, for it was his business to satisfy his customers; and, naturally, if no special requirements were asked of the manufacturer, he did not feel inclined to go to the extra trouble and expense of producing a high-grade product.

"To-day the situation is undergoing a complete change. Neutral sulphate having high-quality physical properties is the order of the day, and the purchaser is far more influenced by mere colour than ever before. The periodical discoloration of sulphate of ammonia, which usually occurs in fitful bursts, without any very obvious reason, is now mainly confined to the small and medium scale producers, who have not as yet seen their way to install the apparatus necessary for turning out a high-grade neutral salt."

In an editorial article, commenting on this paper (*Chemical Age*, December 18, 1920), we read: "Sulphate of ammonia and its vagaries in the direction of colour and quality seem to have been monopolising attention of late. At one time it used to be said that some purchasers of the material really would not object if it consisted of about 50 per cent. of plaster of Paris, so long as it looked like what it was supposed to be. The insinuation may savour of hyperbole, but it certainly used to be a fact that quality, both physical and chemical, counted for little. Like so many others, however, the sulphate of ammonia consumer has progressed with the times. As an instance may be quoted the experience of one of our representatives who, while travelling in the Midlands, got into conversation with an obvious agriculturist, and was particularly surprised to find him fully alive to the importance of nitrogen content, and apparently well informed as to the high nitrogen fertilisers, such as synthetic urea, which the Badische concern is now turning out. An incident such as this serves to emphasise the importance of every sulphate of ammonia manufacturer attending to quality forthwith."

Such unexpected intelligence must, indeed, have been highly disconcerting. A simpler way of overcoming the inconvenience of foreign competition will, however, doubtless be found. "A short Bill . . ."

The Solution of the Nitrogen Problem.

We must now give a brief account of the methods by which the nitrogen problem has been solved. In nearly every case these were based on discoveries by British non-technical chemists, but, as in the case of the aniline-dye industry, the fruits of this work, hardly understood by those in authority, were, on account of lack of business acumen, allowed to pass to more progressive countries for industrial exploitation. Now that the hard spade-work has been done, and the technical success of the processes has been assured by foreigners, the British manufacturer is beginning to wonder if, even at this late hour, he cannot rescue some profit from the forgotten discoveries of his scientific countrymen. Grandiose prospectuses are appearing, in which the virtues of nitrogen fixation are extolled, and chemistry is dimly perceived as a possible source of profit in new fields. The investor may not be altogether forgetful of similar promises put before him a few years ago, and if he is wise he will wish to be assured that the expert guidance of such highly complex scientific undertakings is in the hands of men of science, and that they are not merely distorted and nebulous fancies seen through the spectacles of the financiers. At any rate, he may be spared some disappointment if he does take the trouble to get this assurance.

The fixation of nitrogen as at present carried out on an industrial scale is based on the following processes:

1. The direct union of the oxygen and nitrogen of the air at the high temperature of the electric arc. At this high temperature the nitrogen is burnt by the oxygen to nitric oxide, NO, from which nitric acid is made by the action of air and water. This so-called Arc Process is carried out in Norway, France, Germany, and Switzerland.

2. The direct union of nitrogen and hydrogen under great pressure in the presence of a catalyst to form ammonia, from which nitric acid may be obtained without difficulty by oxidation with air or oxygen in presence of other catalysts. This so-called Synthetic Ammonia Process was developed on a really impressive scale in Germany under the stress of war.

3. The reaction of atmospheric nitrogen with calcium carbide at a high temperature, with the formation of calcium cyanamide, $CaCN_2$, which can either be utilised directly as a nitrogen fertiliser in the soil, or by heating with water under pressure can give ammonia. The latter can be fixed as ammonium sulphate for fertilising purposes, or oxidised to

nitric acid and nitrates. This is the Cyanamide Process, largely used in France, Norway, Sweden, Germany, and America. There are cyanamide works on Canadian soil, but it is perhaps characteristic that they are owned by an American company.

The enormous extension which has taken place in nitrogen-fixation industries may be appreciated from the following table (from the "Statistical Supplement to the Final Report of the Nitrogen Products Committee," H.M. Stationery Office, 1921, 1s. net), showing the actual output of fixed nitrogen in 1912 and the maximum potential capacity in 1920 respectively. The figures refer to world resources.

	1912.			1920.		
Source of Supply.	*Output in Long Tons of Product.*	*Metric Tons of Nitrogen.*	*Per Cent. Total Output.*	*Productive Capacity in Long Tons of Product.*	*Metric Tons Nitrogen.*	*Per Cent. Total Productive Capacity.*
Chile nitrate industry (assuming 95 per cent. product)	2,586,975	111,329	57·5	2,966,061*	471,000	30·2
By-product ammonium sulphate (24·5 per cent. ammonia assumed)	1,229,773	272,007	38·0	2,015,440	413,000	26·6
Cyanamide (18 per cent. nitrogen)	126,538	22,435	3·1	1,777,000	325,000	20·9
Arc products (13 per cent. nitrogen)	75,000	9,907	1·4	290,400	38,300	2·5
Haber ammonia	Nil	Nil	Nil	1,503,000	308,000	19·8
Total fixation ..	201,538	32,342	4·5	3,570,400	671,300	43·2
Grand total ..	4,018,286	715,678	100	8,551,901	1,555,300	100

This table shows that whilst the output contributed by Chile has decrease to half, that of synthetic industries has increased from $4\frac{1}{2}$ per cent. of th whole in 1912 to $43\frac{1}{2}$ per cent. in 1920. The most important fact is th fixation processes are now the largest contributor to the world's requirement In spite of the enormous extensions of the Haber process, the cyanami process is the largest.

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* Maximum war output, 1917.

Besides these three main processes there are many others, but these are still in an experimental stage and cannot be described in the present book. Many of them, paraded with great mystery in patent specifications, are manifestly absurd and impossible, but will no doubt feature in future company-promoting prospectuses.

Before we pass to a description of the existing processes of nitrogen fixation, however, it is necessary to describe the natural sources of nitrogen fixation, since these are at present the sole means of supply of the greater part of the British Empire. These natural sources are Chilean nitre and ammonium sulphate obtained as a by-product of the gas and coke industries—*i.e.*, from coal. A careful consideration of these sources is necessary, because they are at present largely dependent on British capital, and it is therefore of interest to examine carefully their possible future, and the relations between them and the new methods which are being so actively developed. The competition at present between natural and synthetic nitrates is not such as to lead to any great interest on the part of investors or users, but it is unquestionable that it will become fiercer as the new methods are increasingly applied, extended, and improved.

Every process of nitrogen fixation is dependent on cheap power. It is usually assumed that the synthetic ammonia process is an exception in this respect, but the large requirements in cheap hydrogen of that process amount to the same thing as cheap power, since the hydrogen has to be generated by electrolysis of water, requiring electrical energy, or prepared from water gas, in the manufacture of which large quantities of coal are consumed—*i.e.*, potential sources of energy.

It will therefore be necessary to make a brief survey of the sources of energy which are available, and the relation of these sources to nitrogen-fixation industries.

Energy.

It is a commonplace of science that all energy, except an altogether insignificant fraction (which, if the theory of the origin of the earth usually accepted is true, is no exception), is derived ultimately from the sun. The immense stores of coal are the remains of the extinct forests of plants, the tissues of which were built up, as is the case with their modern descendants, only with the co-operation of the solar rays. Green plants imperatively require light for healthy growth. The rushing torrents, and irresistible falls of water, which have been harnessed in a few cases to the needs of man, have their origin also in the heat of the sun. The water of the sea is slowly evaporated by the solar heat, and the moist air, chilled in contact with lofty mountain ranges, deposits its store of water at a high altitude. In its descent from this altitude the water can perform work. This work, however, is derived from the solar heat which raised the water in the first instance. The Norwegian water power is derived from melting snow, but this White Coal was raised to its position of potential energy by the heat of the sun. The energy of the tides, the Green Coal which is now attracting attention, is derived from the rotational energy of the earth, and in utilising this we shall be following the gospel of Protection in its most sublime form. In supplying our needs we shall be applying a brake to the earth.

At present the energy derived from water power in the United Kingdom is an insignificant fraction of the whole. The coal supplies are still not too expensive to utilise, and coal economy is still more talked of than practised. It has generally been assumed that the generation of electrical energy from coal would be too expensive to permit of its use in the fixation of nitrogen. The Nitrogen Products Committee devoted a large part of their report to the consideration of the economical use of coal in the generation of electrical energy. They pointed out that large advances in economy were possible, and expressed the opinion that if the most economical method were adopted, which they considered to be the generation of electrical energy by large-scale direct-fired steam turbo-generator plant, the cost of the energy derived from coal need not be too high to permit of its use in the economical and competitive fixation of nitrogen. The conditions of operation were summarised as follows: "In the production of power for nitrogen-fixation processes it is therefore fundamentally necessary that (*a*) large units of power plant should be employed, so as to minimise the capital cost per kilowatt installed, the coal consumption, and the running cost of the power station; (*b*) the power plant should be operated at a high annual load factor (*i.e.*, a large proportion of the power capacity of the plant should be utilised), still further to diminish the running costs per unit output; and (*c*) the design of the units of power plant should be such that the utmost reliability of supply is ensured."

This is the "Super Power Station" recommendation, which, like so many other "Super" schemes, has aroused a good deal of criticism. Although it would be hard to defend the present system of a crowd of tiny power stations, delivering all possible variations of current—alternating, direct, low voltage, and high voltage—and therefore incapable of co-ordination, the national prejudice against organisation as compared with individual initiative will doubtless hold its own for some time. In any case it may be said that the entirely unexpected turn taken by the coal industries, and the apparently unending upward tendency of the cost of coal, have completely falsified all the calculations of the Committee. It was assumed that coal at 10s. per ton would be possible after the reconstruction period. It may safely be said that it will be a very long time before this hope is realised.

The utilisation of peat, extensive bogs of which exist in Ireland and in other parts of the United Kingdom, has often been attempted. The difficulty to be met is the excessive amount of water in the material, sometimes as much as 90 per cent. The cutting and drying of peat are expensive, and other ambitious schemes have proved total failures. The results so far obtained do not hold out much hope for the successful use of peat on a large scale as a source of power.

The utilisation of the water-power resources of the United Kingdom is a matter much more worthy of consideration. The harnessing of the tides of the Severn has lately come prominently before the public. As far as can be made out, the scheme is part of a project for bridging the Severn for the use of the railway, and there is a good deal more hope of a really useful and economical power plant being established in this way as an afterthought than on the basis of real national economy or benefit. A figure of a halfpenny a unit is quoted by Sir Alexander Gibb; this is very much below the cost by steam generation, but it is still very much higher than the cost in Norway from water power, or in Germany from brown coal.

The establishment of a successful nitrogen-fixation industry in the United Kingdom is dependent on a cheap source of power. At present there is no prospect of such a source at all comparable with those of Norway. The utilisation of water power is a question which, in view of recent movements in coal prices, is attracting a good deal of attention in many countries. In their Preliminary Report, the Water Power Subcommittee of the Conjoint Board of Scientific Societies estimate the world's demand for power at 120 million h.p., utilised as follows: Factories, 75; shipping, 24; railways, 21. Of the power used in factories the United Kingdom takes 13, and the British Dominions 8, million h.p. Only 8·3 per cent. of the *available* water power in the United Kingdom is at present utilised; in Germany 43·8 per cent. is already harnessed. The aggregate potential water power of the British Empire is estimated at 50 to 70 million h.p.

Bird's-Eye View of the Nitrogen Industry.

The whole nitrogen industry is summarised in a table, contained in the Report of the Nitrogen Committee, and reproduced below. In this the different processes are divided into (1) Recovery Processes, including what we have called Natural Sources; (2) Fixation Processes, depending on the direct utilisation of atmospheric nitrogen; and (3) Conversion Processes, in which a direct product of a fixation process—viz., ammonia—is converted into a secondary product, nitric acid, which may be more useful for particular purposes, or absolutely essential for some—*e.g.*, in the making of explosives.

Composition of Nitrogen Products.

The various nitrogenous products contain very different amounts of combined nitrogen, and since the nitrogen content is the principal factor in determining their relative value, the following table may be useful for purposes of comparison. This table is also taken from the Nitrogen Product Committee's Report.

Processes.	*Primary Products.*	*Secondary Products.*
Recovery Processes :		
By-product ammonia.	Crude ammonia liquor or ammonium sulphate, according to the system of recovery adopted.	Other ammonium salts.
Retort or Chile nitrate process.	Nitric acid, dilute (65 per cent.) or concentrated (90 to 96 per cent.), according to the method of operation.	Nitrates—*e.g.*, ammonium nitrate.
Fixation Processes :		
(*a*) The arc process.	Oxides of nitrogen, normally recovered as dilute (30 to 40 per cent.) nitric acid.	Concentrated (93 to 96 per cent.) nitric acid, or nitrates of calcium, sodium, or ammonium.
(*b*) Cyanamide process.	Calcium cyanamide.	Ammonia or ammonium sulphate; nitrate of urea, guanidine, and other organic chemicals.
(*c*) Synthetic ammonia (Haber) process.	Pure ammonia gas or solution.	Ammonium sulphate or chloride.
(*d*) Cyanide processes (various).	Crude sodium, barium, or other metallic cyanides.	Finished cyanides, or ammonia or ammonium salts.
(*e*) Haüsser or Bender processes.	Oxides of nitrogen normally recovered as dilute (30 per cent.) nitric acid.	Concentrated (93 to 96 per cent.) nitric acid, or nitrates.
(*f*) Serpek process.	Crude or pure aluminium nitride.	Ammonia or ammonium salts.
Conversion processes :		
(*a*) Ammonia oxidation.	Oxides of nitrogen normally recovered as dilute (50 to 53 per cent.) nitric acid; concentrated nitric acid (65 to 70 per cent.) or metallic nitrates by the new direct processes (p. 322).	Concentrated nitric acid; nitrates of ammonium, sodium, or calcium; pure nitrogen peroxide (NO_2).
(*b*) Bacterial oxidation.	Dilute solutions of nitrates of calcium or ammonium.	Nitrates of calcium or ammonium.

(*Note.*—The above table has been brought up to date in one or two instances nce its publication in 1920 by the Nitrogen Products Committee.)

NITROGEN CONTENT OF IMPORTANT NITROGEN COMPOUNDS AND PRODUCTS.

Compound or Commercial Product.	*Nitrogen Content per Cent.*	*Tons of Product per Ton Nitrogen.*	*Compound or Commercial Product.*	*Nitrogen Content per Cent.*	*Tons of Product per Ton Nitrogen.*
Sodium Nitrate, $NaNO_3$:			Nitric Acid, HNO_3:		
(*a*) Pure	16·47	6·07	(*a*) 100 per cent. ..	22·22	4·50
(*b*) Commercial (Chile nitre, 95 per cent. purity)	15·65	6·38	(*b*) 96 ,, ..	21·33	4·68
			(*c*) 90 ,, ..	20·00	5·00
			(*d*) 65 ,, ..	14·44	6·92
Ammonium Sulphate, $(NH_4)_2SO_4$:			Sodium cyanide, NaCN, 100 per cent.	28·57	3·50
(*a*) 100 per cent.	21·21	4·71	Potassium cyanide, KCN, 100 per cent.	21·53	4·64
(*b*) 25 ,, ammonia ..	20·58	4·85			
(*c*) 24·5 ,, ,, ..	20·17	4·95			
(*d*) 24 ,, ,, ..	19·76	5·05			
Ammonia, NH_3:			Sodium nitrite, $NaNO_2$, 100 per cent.	20·29	4·92
Anhydrous liquid	82·35	1·21	Calcium cyanamide, $CaCN_2$:		
Concentrated Ammonia Liquor:			(*a*) Pure, 100 per cent. ..	35·00	2·85
(*a*) 25 per cent.	20·58	4·85	(*b*) Raw furnace products	20·00 19·50	5·00 5·12
(*b*) 35·6 per cent. (sp. gr. 0·88) ..	29·31	3·41	(*c*) Nitrolim	18·00 17·50 16·00	5·55 5·71 6·25
Crude Gas Liquor, 10 oz. strength (2·17 per cent. ammonia)	1·78	55·95			
Potassium Nitrate, KNO_3, pure, 100 per cent.	13·86	7·21			
Ammonium Nitrate, NH_4NO_3, pure, 100 per cent.	35·00	2·85			
Calcium Nitrate, $Ca(NO_3)_2$:					
(*a*) 100 per cent.	17·07	5·86			
(*b*) Commercial	13·00	7·69			

It must be noted in connection with this table that the combined nitrogen content is not the only factor determining the utility or value of a material for industrial or agricultural purposes. In particular, the fertilising value of combined nitrogen varies according to the state in which it is present. It is generally admitted that nitrate nitrogen is of the greatest value for fertilising purposes, as all the other forms have first to be converted into nitrate nitrogen before assimilation. The conversion of ammonia or cyanamide nitrogen, however, takes place so easily in the soil, by the action of bacteria, that the differences are very small. The various kinds of combined nitrogen may be classified as follows:

I. *Nitrate Nitrogen:* Existing as Nitric Acid, HNO_3, or its salts, the Nitrates—*e.g.*, Sodium Nitrate (Chile Nitre), $NaNO_3$, Potassium Nitrate (Saltpetre), KNO_3, Calcium Nitrate, $Ca(NO_3)_2$, and Ammonium Nitrate, NH_4NO_3 (this also contains Ammonia Nitrogen).

II. *Nitrite Nitrogen:* Existing as Nitrous Acid, HNO_2, or its Anhydride, Nitrogen Trioxide, N_2O_3, or its salts, the Nitrites—*e.g.*, Sodium Nitrite, $NaNO_2$, and Calcium Nitrite, $Ca(NO_2)_2$.

III. *Ammonia Nitrogen:* Existing as Ammonia, NH_3, or Ammonium Salts—*e.g.*, Ammonium Chloride, NH_4Cl, Ammonium Sulphate, $(NH_4)_2SO_4$, or Ammonium Nitrate, NH_4NO_3.

IV. *Cyanide Nitrogen:* Existing as Hydrocyanic Acid (Prussic Acid), HCN, and its salts, the Cyanides—*e.g.*, Potassium Cyanide, KCN, and Sodium Cyanide, NaCN.

V. *Cyanamide Nitrogen:* Existing as Calcium Cyanamide, $CaCN_2$, Barium Cyanamide, $BaCN_2$, and as free Cyanamide, NH_2CN, formed by the action of moisture on the metal cyanamides.

VI. *Other Forms:* These include such products, natural or artificial, as Alkaloids (*e.g.*, Quinine, Strychnine, Morphine, Hyoscine), Dyes (Indigo, etc.), Drugs (Antipyrine), Explosives (T.N.T., Picric Acid). With these forms we shall not be concerned; their preparation is not connected directly with the Nitrate Industry, although many of them cannot be made without supplies of Nitric Acid or other Nitrogen Compounds.

Of all the forms of combined nitrogen, ammonia nitrogen from gas and coke-oven liquor and from blast furnaces, and to a very limited extent cyanide nitrogen, are the only ones produced in the United Kingdom. The whole of the by no means small requirements of the country in nitrates, and in cyanamide, are supplied by foreign countries as imports. The most important is nitrate in the form of Chile nitre; other products such as guano and potassium nitrate are imported in relatively small quantities. The commanding position in the nitrogen supplies of the world before the war was held by Chile, and although synthetic processes have during and since the war been developed on an immense scale, Chile still remains an important source of the world's supply of combined nitrogen. We shall therefore commence our detailed description of the nitrogen supplies by a reasoned consideration of the part played by Chile, and its possible future.

Sodium Nitrate (Chile Saltpetre), $NaNO_3$.

As a most efficient manure, the agricultural value of this important salt has long been known, but the discovery of naturally occurring deposits only dates back some one hundred years.

It sometimes occurs in natural and artificial accumulations in association with potassium nitrate, but by far the most important sources of the salt are the famous beds found in Chile and Peru and along the coasts of Bolivia. There is little prospect of any other extensive deposits of sodium nitrate being discovered, as owing to its solubility the substance can only accumulate in rainless districts. Outside Chile such districts are few, and apart from some unexplored deserts it is difficult to see where any large quantity of the material can exist.

The nitrate district of Chile starts in the north at Hazpampa, and runs south parallel to the coast to Lagunas. Behind the seaboard ports, such as Pisagua, Iquique, etc., the coast hills rise abruptly to a height of about 3,000 feet. Further inland the hills give place to the level and desert pampas, which extend eastward to the foothills of the Cordilleras or Andes. The nitrate-bearing material is found on the eastern slopes of the coast hills, particularly towards the Pampas de Tamarugal and the desert of Atacama, at a height of from 3,000 to 5,000 feet above sea-level. The beds lie from 10 to 45 miles inland, and are found mostly in valley cavities. The nitrate-grounds form a long, narrow strip, on the average some 2 to 3 miles in width, in a rainless region devoid of vegetation. An examination of a typical bed worked for nitrate will in general reveal the presence of the following layers, mentioned in order from the surface downwards:

1. *The Surface Layer, or Chuca.*—A layer of gypsum sand containing rough pieces of a greyish material largely consisting of anhydrous calcium sulphate, and known as "loza." This layer may be from 8 to 10 inches thick.

2. *The Costra.*—A rocky conglomerate in which clay, gravel, fragments of porphyry, felspar, etc., are cemented together by the sulphates of calcium, potassium, sodium, and magnesium, together with a little sodium chloride. The costra may extend to a depth of some 6 to 10 feet.

3. *The Congelo.*—A layer of which the predominating constituents are the chlorides of sodium and magnesium, some sulphates, and even a little sodium nitrate.

4. *The Caliche,* the real nitrate-bearing earth, is found beneath the congelo, and is a layer varying in thickness from 1½ to 12 feet. The caliche is largely composed of sodium nitrate, and is the material primarily worked up for this salt.

5. *The Coba.*—A clay bed upon which the caliche rests, and which is itself in contact with the primitive rock. No nitrate is found beneath this layer.

Grades of Caliche.—There are considerable variations in the nature and depth of these layers, particularly in the southern districts. The content of sodium nitrate in the caliche varies considerably, and caliche may be divided roughly into three grades: (*a*) The first quality, containing 40 to 50 per cent. and even up to 80 per cent. of sodium nitrate; (*b*) the second quality, with 30 to 40 per cent.; and (*c*) the third quality, with between 17 and 30 per cent. of sodium nitrate.

A good ground would possess a bed of caliche 3 to 4 feet thick and containing 40 to 45 per cent. of sodium nitrate

$NaNO_3$. There is a possibility that sooner or later material with even less than 17 per cent. sodium nitrate (grade c above) will be worked economically, as methods of extraction, plant design, etc., are evolved and improved upon.

Caliche is sampled locally by throwing a pulverised portion on to an incandescent tinder. Material with a content of less than 5 per cent. of nitrates does not give sparks; with that containing from 6 to 10 per cent. the sparks are barely visible; from 10 to 20 per cent. the sparks are more visible and numerous; and with 20 to 30 per cent. the sparks are visible in full sunlight. The presence of over 35 per cent. nitrates is indicated by deflagration and flame.

The following are typical analyses of caliche, I. being a sample of an extensive deposit as given by Forbes (*Phil. Mag.*, 1866, **32**, 135), and II. a sample of the material worked by the Oficina Ramirez (Harvey, *Proc. Inst. C. E.*, 1885, **82**, 337):

	I.	II.
Sodium nitrate	21·01	51
Sodium chloride	55·27	26
Sodium sulphate	4·74	6
Calcium chloride	0·33	—
Potassium iodide	0·87	—
Aluminium sulphate	9·81	—
Magnesium sulphate	5·93	3
Insoluble matter	2·04	14
Moisture	—	—
Total ..	100·00	100

Donnan (*Chem. Age*, November 29, 1919, **1**, 634) gives the composition of the beds as follows: Sodium Nitrate, 14 to 30 per cent., normally 25 per cent.; Potassium Nitrate, 2 to 6 per cent., normally 3 per cent.; Sodium Chloride, 8 to 25 per cent. Insoluble residue (clay, gravel, and sand), 25 to 50 per cent. Present in small amount only: Calcium Sulphate 2 to 6 per cent.), Sodium Sulphate, Magnesium Sulphate. Present in traces only: Borax (1 to 2 per cent.), Iodate (0·1 per cent.), Perchlorate, Chromates, Vanadates, etc.

Newton (*J. S. C. I.*, 1900, 408) gives the following analyses of caliche and costra:

	Caliche.			*Costra.*	
	1	2	3	1	2
Water	2·322	1·983	2·547	4·122	3·653
Sodium nitrate*	50·046	39·322	28·503	13·626	12·260
Potassium nitrate* ..	0·454	4·800	4·512	3·017	2·963
Sodium chloride	25·272	26·912	21·993	18·952	20·820
Sodium sulphate	5·204	2·540	2·786	4·990	5·504
Calcium sulphate ..	2·720	3·064	5·032	7·203	7·682
Magnesium sulphate ..	0·326	5·022	4·544	6·606	4·593
Calcium phosphate ..	None	Trace	0·312	0·223	0·262
Potassium iodate† ..	0·022	0·101	0·073	0·076	0·096
Ferric oxide and alumina ..	3·200	1·853	2·270	3·836	3·920
Silica	10·434	14·403	27·428	37·349	38·247
Total ..	100·000	100·000	100·000	100·000	100·000
* Total nitrates	50·500	44·122	33·015	16·643	15·223
† Containing iodine ..	0·017	0·078	0·057	0·059	0·071

Another analysis of the best quality of caliche is as follows:

Sodium nitrate	50	Sodium iodate	1
Sodium chloride	26	Sodium nitrite	
Sodium sulphate	6	Magnesium chloride	
Magnesium sulphate ..	3	Hydrochloric acid	
Insoluble	14	Magnesium nitrate	

According to F. Dafert (*Monats.*, 1908, **29,** 235; abst. *J. S. C. I.*, 1908, **27,** 684), chemical examination of eight specimens of "caliche" from widely different sources showed that in all cases the portion soluble in water contained calcium, magnesium, potassium, sodium, nitrate, chloride, sulphate, and iodate. In most cases perchlorates also were present; and in the two specimens richest in nitrates small quantities of chromates were found. In no case did the soluble portion contain bromide, borate, nitrite, ammonia, carbonate, phosphate or iodide. The specimens richest in sodium nitrate contained also much potassium nitrate. Different views as to the cause of the presence of iodate and perchlorate are discussed the author being inclined to the hypothesis that iodate and periodate are produced by the action of the higher oxides of nitrogen, or of their unstable compounds, with ammonia, or iodide, and perchlorate by the oxidation of chloride by iodate Perchlorate is usually considered to be a plant poison.

Formation of the Chilean Nitrate Deposits.

Many theories have been advanced to account for the formation of these nitrate deposits, which in their way are unique. Unanimity has by no means been reached on this question, and it would appear that considerable and systematic geological and chemical research will yet be necessary before a final opinion can be given.

The deposits do not form beds of any definite character, but represent the outcrop of a bed of salt which appears to have been left at the bottom and sides of ancient tidal lagoons by the upheaval of the coast. Guano, fish remains, and other substances of marine origin, abound.

1. One theory regards the nitrate as the product of the decomposition of organic matter in the presence of calcium carbonate and the salt left by the evaporation of sea water. This view receives a certain amount of support from the presence in the deposits of sodium iodide and iodate, and of salts of magnesium and calcium, all of which occur in sea water; but it should be remembered that the presence of these salts may be quite well accounted for by land washings, as in the case of other inland salt lakes. The nitrification seems to have occurred only at the outcrop of the salt, for the content of sodium nitrate diminishes towards the middle, and practically vanishes at the centre of the deposit.

The absence of bromide, however, is evidence against the evaporation of an inland sea, since bromides are always present in sea water, as is also the fact that the stones in the caliche are sharp and jagged, showing no signs of being water-worn. The absence of phosphates also rather discounts the idea that guano may have been the substance primarily responsible for the formation of the nitre, since guano is rich in phosphates.

2. Another possible theory is that in past geological ages this area was a centre for violent thunderstorm conditions, and oxides of nitrogen are supposed to have been produced in the atmosphere, being subsequently fixed as nitrates in underground drainage systems.

3. Nitrifying bacteria may be responsible for the formation, the temperature and basic ingredients of the soil rendering this

possible. The nitre might be expected to accumulate owing to the absence of vegetation for its assimilation. The concentration of the deposits on the eastern slopes of the coast hills may be regarded as the effect of the flushing of the soil from the foothills of the Andes throughout the width of the Tamarugal valley. The coast hills form a barrier to the further passage of the washings, which evaporate and deposit their saline contents.

Extraction.

The separation of sodium nitrate from the raw caliche has been the subject of much study and experiment, particularly of recent years. During the first half of the nineteenth century the only material worked was that containing over 50 per cent. of nitrate. The caliche was boiled with water in open direct-fired tanks, the solution being transferred to settling tanks, where the insoluble matter and the sodium chloride were deposited. The solution was then allowed to crystallise in the "bateas." The residue in the settling tanks, which was frequently discarded, contained 15 to 25 per cent. of nitrate. In 1856 the method of steam heating for the dissolving tanks was introduced, and the mass was agitated by the injection of live steam under a pressure of about 50 pounds per square inch. Later, indirect steam heating was introduced. These processes resulted in the accumulation of much waste material, which in reality contained appreciable amounts of unextracted nitrate.

The Shanks Process, introduced in 1876, and still almost universally employed, facilitated the treatment of poorer material than was up to that time generally worked, and was then an undoubted advance on any other method of extraction in use.

The chuca dust is cleared away, and a round hole about 9 inches in diameter is cut vertically through the costra and caliche. When the congelo is reached the hole is enlarged to cup form, the cavity being filled with gunpowder, to which is connected a slow match to the surface. The hole is then well tamped with debris, the charge is fired, and a good explosion will cause the ground for yards around to be split up and broken. The blocks are loosened with crowbars and the bigger lumps broken up, the costra overlayer being separated from the caliche. The trench is then worked forward by another explosion, being filled in behind with the costra to form a cart track. The material is sorted, classified, and placed in heaps by the workmen, and is then transported to the nitrate works by mule carts or railway wagons.

The nitrate is extracted from the crude material by boiling with water, the boiling tanks being built on a hill as near the centre of the grounds as possible. They are elevated in order to allow the solution of nitrate, or "caldo," to run down into the crystallising tanks and to give a good shoot for the residue from the lixiviation ("ripio"). There must also be sufficient fall for the condensed steam of the coils to run back to the steam boilers. For good working the bottom of the boiling tanks should be about 12 feet above the top of the steam generators.

The raw material is dumped in lumps of about 1 foot diameter, and is then crushed to pieces of 2 to 3 inches in diameter. Finer crushing is not advisable, as the caliche in the boiling tanks would then lie too close to allow the water to circulate thoroughly through the mass.

A typical boiling tank would be some 32 feet long, 9 feet deep, and 6 feet wide, and a 5-inch steam pipe forms a coil about 9 inches from the sides, making the circuit of the tank five times. Steam is let in at the top, the condensed water flowing out at the bottom. The coal used in raising the steam amounts to about 1 ton for every 7 tons of nitrate produced. The tanks are constructed of ½-inch iron plate, and are fitted with a false bottom in the form of an iron grid about 1 foot above the real bottom. This grid serves to support the caliche.

There are two doors at the bottom, which are opened from the outside during the clearing out of the spent material. The tanks are strengthened by cross-bars from side to side. From below the false bottom one opening is arranged to allow the caldo, or hot nitrate liquor, to pass by means of curved iron troughs down to the crystallising tanks, and another lower one allows the "relave," or last washing, to run out to the relave tanks or reservoirs.

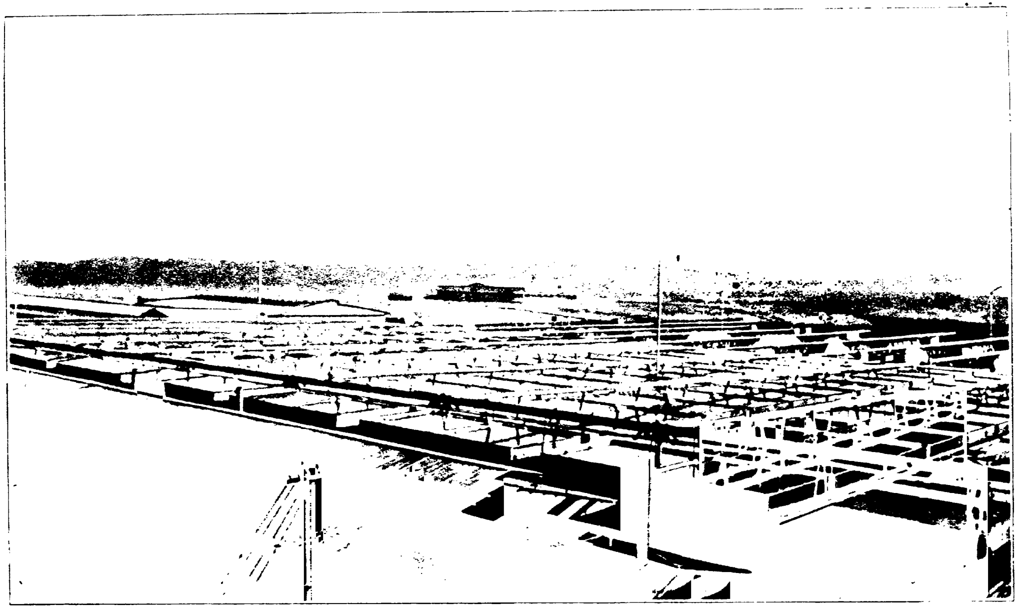
The charge for each tank is about 60 to 80 tons of caliche, and the tanks are worked in batteries of six or eight, communicating by a 9-inch pipe. The exhausted caliche is cleared from the last tank of the series by hand into trucks, in the form of a liquid mud which afterwards sets hard like cement. Much space has to be left for the accumulation of these ripio heaps. The next tank in the series contains nearly spent caliche having its last washing with fresh water. After standing some hours this water is run off by the relave vent and carried to one of the relave reservoirs near the lixiviation tank. When all the water has been run off, this tank is treated as a ripio tank described above.

The next tank contains partially extracted caliche, on which relave water is allowed to run. When this water has been allowed to stand for a few hours the liquids are passed from one tank to the next. Plain water is run in from the top, forming a layer on top of the heavier relave water, which is gradually passed down through the false bottom and up the 9-inch connecting pipe to the top of the next tank. This operation will, of course, drive forward the still more enriched liquor in the tanks higher in the series.

In the second, third, and fourth tanks of the series, containing richer caliche, the liquor is heated by means of the steam coils.

In the first tank of the series the liquor is boiled at 120° C. by means of steam at 50 pounds pressure passing through the coils. In due course the steam is turned off and the suspended matter allowed to settle. In the manufacture of a product containing over 90 per cent. nitrate and 1 per cent. or less of sodium chloride, the liquor is first run into tanks called "chulladores," just below the level of the boiling tanks. The former are about 15 feet by 9 feet, and 3 feet to 6 feet in depth, and have a capacity sufficient to treat all the saturated liquor obtained during twenty-four hours. The time allowed for settling is normally from ten to twenty minutes. The addition of such substances as aqueous ammonia, lime water, glue, etc., will accelerate the deposition of solid matter. The operation is regarded as finished when incipient crystallisation of nitrate is observed on the surface of the liquid. Here a further deposition of suspended matter takes place, and the clear liquor is transferred to the "bateas," or crystallising tanks, where it is allowed to cool and crystallise for about a

PLATE I.



GENERAL VIEW OF "BATEAS" OR CRYSTALLISING TANKS.

week. For the production of a less pure product the liquor is run straight from the boiling tanks to the bateas. Views of these crystallising pans are shown in Plates I and II.

The caldo as run off contains up to 80 pounds of nitrate per cubic foot; the mother liquor from the crystallising tanks, known as "aqua vieja," is drained away to reservoirs. and may contain up to 40 pounds of nitrate per cubic foot. It may be treated for the recovery of its iodine content, and in the process of boiling the caliche is returned to the boiling tanks. Fresh water has to be added to replace that lost by evaporation and leakage, and is also necessary for the final washing, in order that nitrate liquor may not be turned to waste with the ripio. The total water requirements of an oficina may amount to 6 gallons per cwt. of nitrate made.

Sodium chloride is less soluble in hot water than in cold in the presence of nitrate, the solubility decreasing as the content of nitrate increases. This results in the deposition of sodium chloride in the apparatus, and it is attempted to localise this deposition in special receptacles by forcing the liquid rapidly through the connecting pipes, etc.

A crystallising tank is formed of 6-inch iron plate, 25 feet by 18 feet, and 2 feet 9 inches to 3 feet 3 inches deep. There is a slope to the bottom for the purpose of draining off the mother liquor when crystallisation is complete. The time required for this is about five to six days, and forty-four tanks are required for each battery of six boiling tanks. The nitrate is allowed to drain after the removal of the mother liquor, and is then put into cars and transferred to "cauchas," or drying floors (Plate III), where it is allowed to remain further for about five days. Its water content on arrival is about 10 per cent.; after drying the analysis* of the crystals is:

	First Quality.	*Second Quality.*
Nitrate of soda	96·50	95·20
Sodium chloride	0·75	2·50
Sulphate of sodium	0·45	0·60
Moisture	2·30	1·70

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* Newton, *loc. cit.*

Modern Refinements.—Under modern conditions there is no doubt that the Shanks process is expensive and inefficient, owing to the fact that in the caliche treated the nitrate content may fall as low as 17 per cent., and the insoluble matter may be as high as 60 per cent. This results in more water being required for leaching purposes per unit of nitrate extracted, and also in greater fuel consumption. The efficiency of recovery averages about 50 per cent. In some works the finely divided material is separated either by dry classification before treatment with the solvent liquor, or as a mud after such treatment. The saturated solution of nitrate is separated from the mud by allowing the mud to settle in tanks with conical floors, or by filtration. In the Butters system the type of filter used is one having a large number of flat filter leaves immersed in the hot liquid. The solid matter is deposited on the leaves by internal suction, and is then detached by the application of internal pressure.

According to A. Allen (*Eng. Mining J.*, 1917, **103,** 230), the caliche is hand-picked and all fines are rejected. It is then carted to central loading stations and crushed to a size suitable for trucks. The caliche is delivered to the leaching vats in gable trucks. The vats are rectangular and hold about 80 tons. Each tank has a filter bottom and is lined with steam coils. The solvent liquor used is the mother liquor from the crystallising tanks, and is so circulated that the nitrate content of the liquor is gradually enriched by passage from one vat to another. After the liquor is drawn off to the settling tanks, the vat contents are washed with cold water, and the residue left is discharged into trucks and dumped. Vast quantities of slime accumulate under the filter-plate of the tanks, and this carries away a considerable quantity of the nitrate. The strong liquor is tested at every stage of the process with the hydrometer. When the density has reached the satisfactory value, the liquor is drawn off into settling tanks, and the clear liquor is decanted by siphon pipes from these. Lime and guano are used as coagulating agents. The decanted liquor goes to the crystallising tanks, where it is allowed to cool. The stage at which to decant the mother liquor is ascertained by sounding the crystallising tank to ascertain the depth of the crystallisation. The crystals of nitrate are allowed to dry and shovelled into trucks and tipped to the sacking house The sodium chloride occurring naturally with the caliche is deposited to a considerable extent with the slime in the leaching vats, but a portion goes to the crystallising tanks Approximately one-half the nitrate produced is known as "95 and 1 per cent." or "refined" nitrate. This means that the shipped product contains at least 95 per cent. of mixed potassium and sodium nitrates, and less than 1 per cent. of sodium chloride.

In the Agua Santa Works the fines (11 per cent. nitrate content) are mixed with liquor (150 grammes of nitrate per litre) in the proportion of 3 of solid to 1 of liquid. The hot pulp is then filtered in the Butters vacuum filters, and a certain proportion of liquor is extracted in this way. This liquor is of varying strength, depending on the amount and the strength of the weak liquor which is used for the extraction, and on the proportion and richness of the raw materials used with it. The filter cakes are subsequently washed twice with weakening liquors.

The washing is claimed to be by displacement only, and the final wash is done with salt water (saturated brine), which leaves the cakes with about 0·23 per cent. nitrate of soda. The cakes are then discharged.

The different liquors obtained from each successive displacement wash are used in the next round, the whole forming a cycle of operations, at one end of which the strong liquor is removed, while at the other end the cold brine "displacement" wash takes place.

As used at present, the Butters process acts in an auxiliary capacity to the main Shanks process, and in this capacity has attained a certain success. The whole of the crushed product is screened in order to remove 20 per cent. of it as fines passing a 6-millimetre mesh. These fines are treated in the Butters filters, the resulting liquors being introduced into the Shanks system, while the coarser material alone is treated in the boiling tanks as formerly. The judicious combination of the Shanks system, the Butters fines treatment, and the use of evaporators, enables material of 14·5 per cent.

nitrate content to be worked successfully with an efficiency of 64 per cent. A diagram of the operation is shown in Fig. 1 (see Hobsbawn and Grigioni, *J. S. C. I.*, **36,** January 31, 1917).

*The Gibbs Process.**—This is a process of extraction which has been elaborated as a result of many experiments carried out on both a laboratory and a technical scale during the period 1912 to 1917. Reports on the success of this type of plant as operated in Chile vary, but it would seem that fairly satisfactory results may be obtained if the engineering design is on an adequate scale.

The object of the Gibbs process is to procure the complete lixiviation of the raw material and the separation of the liquid from the solid by a process of classification and partial filtration. The purpose of the classification is the elimination of the greater portion of the insoluble matter from the caliche, washed free from nitrate; filtration is used solely as a means of treating that portion of the insolubles which cannot be freed from liquor by such simple mechanical means as settling and decantation.

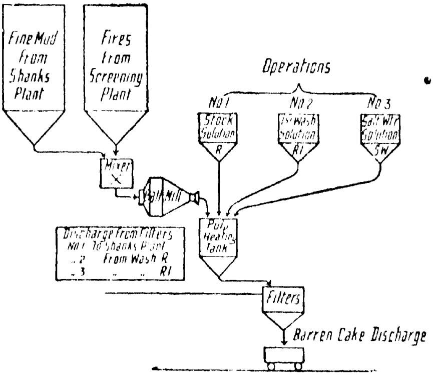

FIG. 1.

The process does not aim at the production of a liquor which will crystallise nitrate direct, but relies on further evaporation to produce a complete separation of the salt.

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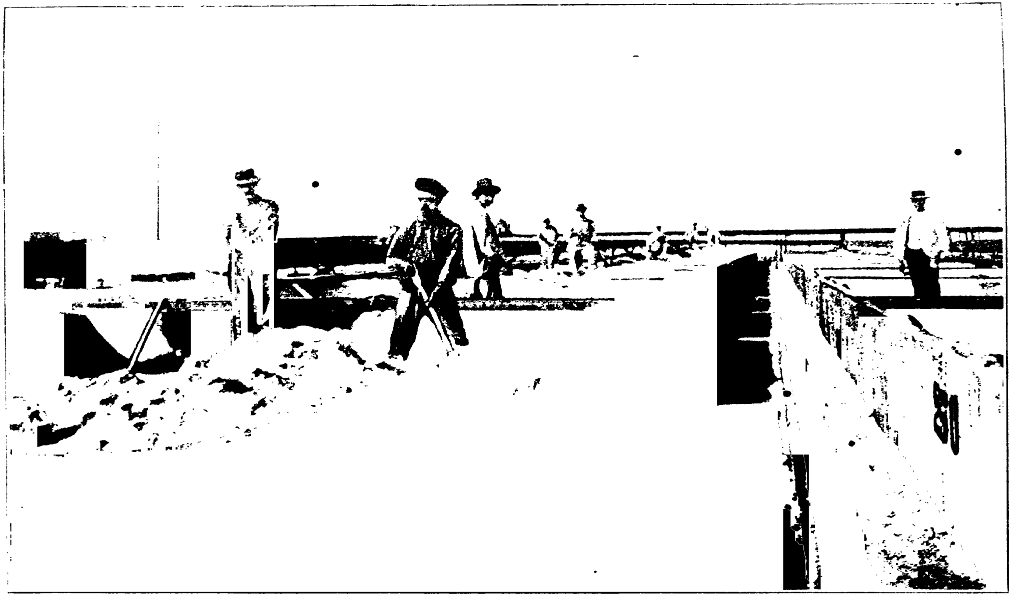
* See pamphlet by Hobsbawn and Grigioni, printed by the *South Pacific Mail*, Valparaiso, 1917.

PLATE II.



NEAR VIEW OF "BATEAS" OR CRYSTALLISING TANKS, SHOWING CRYSTALLISED SALT AFTER REMOVAL OF MOTHER LIQUOR.

To face p. 44.

Lixiviation.—The sands and clays present in raw caliche vary both in grain and composition, and the dissolution of the nitrate allows the insoluble materials to fall apart, forming a mass consisting of solution and sands, stones and clays. This mass is known as " borra."

The Gibbs process of lixiviation is dependent upon its ability to separate the small quantity of the clay from the stones and sands, the result being a coarse product from which the liquor may be easily drained, and which it is easy to wash free from adherent liquor.

By this means, known as " wet classification," the slimes are carried away from the rest of the solid material by the nitrate solution, and are removed from the latter by subsequent settling or filtration. The slimes, forming 10 to 14 per cent. of the weight of the insolubles, are the only part of the solids that need the treatment of filtration.

The aim is a disintegration of the conglomerate and not a grinding of the material. This disintegration is brought about, together with the dissolution of the soluble binding agents, by causing the solid lumps to rub against each other in a slowly revolving mill while in the presence of the solvent. The disintegrating mill merely mixes the solid and solvent together, and it is the solvent action, combined with the rubbing of the pieces together, which brings the mass to the state required in the minimum time. The solvent is a weak solution of nitrate; the mechanically assisted dissolution and disintegration is quite rapid and complete.

The solid may be fed into the mill in lumps, the size of which depends on the original hardness of the materials under treatment. A soft sandy caliche, which easily resolves itself into " borra " on contact with liquor, need not be broken down in the crushers to the same extent as one which is impervious to water.

The caliche is mixed with warm or hot weak liquor on being fed into the mill, the quantity and temperature of such liquor being decided upon by the strength of final liquor aimed at. Usually a liquor is produced containing about 450 grammes of nitrate per litre at a temperature of about 50° C., which conditions are considered the most suitable and economical.

Classification.—In the Gibbs process a separation of the heavier and lighter solid particles is brought about by the use of a Dorr classifier, a diagram of which is shown in Plate IV.

The mixture of sands, slimes, stones, and liquor, in the form of a mush, is allowed to run into the deeper end of the inclined tank, where the heavier solids, as they sink to the bottom, are raked up the incline by the mechanically operated rakes. This heavier mass is drained in its progress to the top of the incline, part of which is above the level of the liquor. On discharge from the classifier it contains about 15 per cent. by volume (on the dry solid) of adherent liquor containing 450 grammes of nitrate per litre.

The liquor, overflowing at the deep end of the classifier, carries with it the slimes and some of the finest sands, the type of separation being governed by the amount of agitation caused by the rakes. Deposition takes place in a settling tank, where a Dorr thickener is used for procuring the required consistency of the slimes. The thickened slimes are withdrawn from the bottom of the tank and filtered, the filtrate being passed to the evaporators. A diagram of the Dorr thickener is shown in Plate V. The solids removed from the classifier pass in counter-current to water through a series of three other classifiers, and the liquor issuing from the first classifier in the series is used for the solution of the nitrate contained in the solids in the disintegrating mill, after passage through a tubular heater maintained at the right temperature. The solids discharged from the last classifier in the series contain about 15 per cent. of water and practically no nitrate.

The general scheme of operation is shown diagrammatically in Fig. 4.

Evaporation.—The evaporation has been designed to be used as a double, triple, or quadruple effect vacuum pan system. Two, three, or four evaporators, as the case may be, are arranged to work together, only one of them being a direct boiler steam-fed effect. The condensed steam from all effects, except the boiler steam from the first, which returns to the boiler, is used to supply the hot water for the lixiviation process.

In the Shanks process the nitrate solution is caused to dissolve more nitrate from the raw material, by raising the temperature, but without (theoretically) the loss of water in the form of steam.

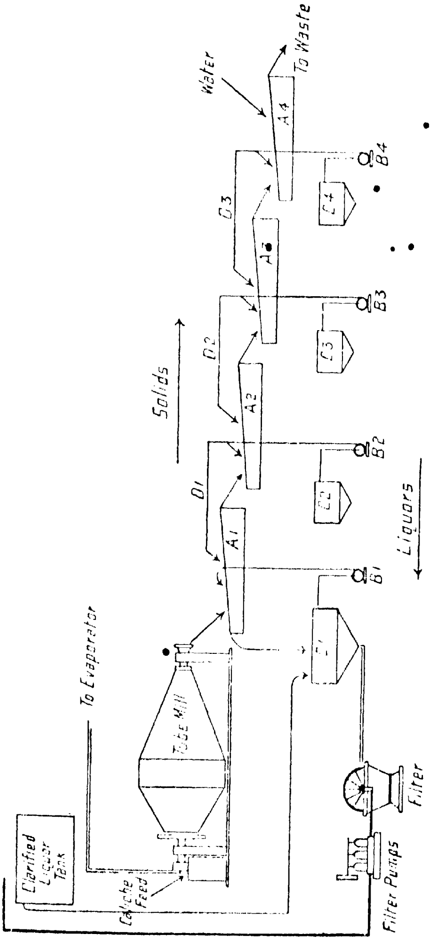


FIG. 2.—GIBBS'S PROCESS.

General scheme: A_1, A_2, A_3, A_4, classifiers; B_1, B_2, B_3, B_4, pumps; C_1, C_2, C_3, C_4, thickeners; D_1, D_2, D_3, discharges.

In the Gibbs process the solution is concentrated by the direct evaporation of water, and no nitrate is added to the liquors at all. The salt is deposited in the evaporator during the concentration.

The Gibbs evaporator has been designed (in conjunction with the Kestner Evaporator and Engineering Company of England) to handle the problem of evaporating liquors which, during the boiling off of water, precipitate salt or other comparatively less soluble salts. It has been called a "salting" type evaporator, and several very large installations of this type of evaporator are in use to-day in England, France, Italy, and Norway.

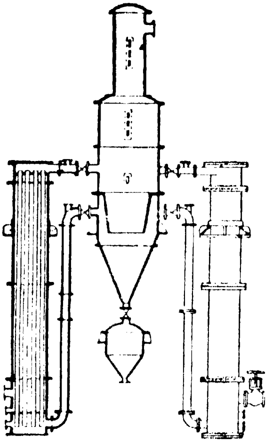
The evaporator is designed to act continuously, and in order to bring this about the calandria (the chamber which contains the tubes in which the liquor is boiled by steam from the boilers passing outside the tubes) is separate from the "separator," the chamber which holds the body of concentrated liquor and in which the precipitated salt and concentrated solution separate by settling.

These heating chambers are arranged in duplicate or triplicate—*i.e.*, one separator may be connected to one, two, three, or even more calandrias. The object of this is to allow for continuity of work by shutting off one and working with the duplicate, should one calandria get out of order by the tubes becoming encrusted with salts or other solids, or become otherwise defective. The calandria is also constructed in such a form as to allow of easy replacement of tubes when any become defective, and of easy washing and cleaning of tubes when encrusted. On account of the extreme length of the tubes the heating surface is very great, and the liquor passes through them, in consequence, at a very high velocity, which considerably reduces the chances of incrustation.

The liquor itself acts as a very efficient scouring agent, and helps to keep the tubes clean.

Shortly after entering the heating tubes the liquor boils, and a mixture of concentrated liquor, precipitated salt, and steam passes out of them and enters the separator shown in the centre of Fig. 3. In this chamber the steam separates from the liquid which collects in the body of the separator, the former being collected and removed and used as the heating agent in the other stages of the multiple-effect system.

The separator is designed to be of very large capacity compared with the quantity of liquor entering it from the calandria, so as to be unaffected by this in so far as the settling of the salts is concerned. That is, the entry of the mixture of steam, liquor, and salt from the calandria, and the overflow of the clear concentrated liquor from the separator to the next effect, can be going on continuously, at the same time preserving the stillness, necessary for efficient settling, in the large body of liquor in the separator itself.



KESTNER PATENT
SALTING TYPE EVAPORATOR

FIG. 3.

The salt, which settles in the coned part of the separator, is removed and washed, and the wash liquors are returned to the feed liquor tank, while the liquor itself is removed to the next stage of the system for further evaporation or for crystallisation by cooling.

The mass of crystals and liquor, as removed from the separator, will be warm, and before the nitrate can be dried in the centrifugal driers it must be cooled to the ordinary temperature. For this purpose the mass is made to pass through a cooled revolving drum or cylinder, which brings about the completion of the crystallisation. The cooled mass is fed into the centrifugal driers, where the crystals are freed from adherent liquor. The nitrate is then ready for sacking, and the liquor which has been removed from it is returned to the evaporator, to the high temperature effect.

This liquor, which passes out with the nitrate crystals, is only sufficient in quantity to enable the latter to be handled through the operations in which it is further cooled and removed to the centrifugals. At the same time it will carry off in solution not only the small quantity of salt which may not have been precipitated during the evaporation process, but also those other salts which will neither precipitate with the salt nor crystallise with the nitrate.

In time this liquor will become overcharged with these other salts, and it will become necessary to subject it to some purifying operation which will remove these salts. Periodically, also, the iodine can be separated by the means usually adopted.

It will be seen that no liquor goes back to the lixiviation section from the evaporation section.

The Gibbs process is estimated to be able to recover in marketable form 90 per cent. of the nitrate content, in raw material with 10 per cent. nitrate content—in other words, that the process is estimated to be 90 per cent. efficient. This figure of 90 per cent. efficiency is, of course, based on nitrate contents, calculated from definitely ascertained weights of raw materials and from analyses performed on representative samples.

Eduardo Charme's process of extraction is said to consist of "a chemical reagent which precipitates the nitrate without the use of heat," a discovery which, it is claimed, "will not only revolutionise the production of Chilean nitrate, but will also reduce its cost by more than 50 per cent." Charme estimates that with the new process the production of 100 kilogrammes of nitrate will cost 65 centavos of Chilean currency (about 6½d.), not including the cost of the extraction of the caliche or raw product and other expenses incurred up to the time of shipment. The cost of manufacture by the new process will be 80 per cent. lower than by the old method, and bearing in mind other expenses which cannot be eliminated, the net reduction in cost will be in excess of 50 per cent. These claims, of course, are of great interest, but they are vague in the extreme, and it must not be assumed that they have yet been commercially established (see *Chem. Age*, October 18, 1919, p. 505).

Extraction of Iodine.—The amount of sodium iodate left in the mother liquor may amount to 3 to 7 grammes per litre, and iodine is recovered from this by treatment with sodium bisulphite, prepared by the reaction between sodium carbonate and sulphur dioxide.

The reaction involving the liberation of iodine occurs in stages :

$$(1)\ NaIO_3 + H_2SO_4 = NaHSO_4 + HIO_3.$$
$$(2)\ 2HIO_3 + 5H_2SO_3 = I_2 + 5H_2SO_4 + H_2O.$$
$$(3)\ I_2 + H_2O + H_2SO_3 = 2HI + H_2SO_4.$$
$$(4)\ HIO_3 + 5HI = 3H_2O + 3I_2.$$

The iodine sludge obtained after settling is pressed in calico bags to free it from liquid, the resulting cakes containing 70 to 80 per cent. of iodine. The impurities consist of calcium sulphate, boric acid, silica, and organic matter. The iodine is purified by volatilisation in iron retorts lined with cement, being condensed in specially constructed stoneware pipes which allow water to drain out. It is packed in small kegs. It is reported that, in order to maintain a high price for iodine, only a limited amount of this is extracted from the Chile nitre mother liquor, the rest being thrown away.

The extraction of iodine is controlled by a Chilean association known as the Combinacion de Yodo, at Iquique, which is regulated by a set of by laws of a most comprehensive character. It regulates the sale of iodine (export), the extent of the participation of each member in the sales, consignment contracts, arrangements with producers in other countries, and propaganda. The only competition with this organisation is the recovery of iodine from seaweed in Japan, France, Scotland, Norway, and the United States, and the bulk of the iodine on the market is of Chilean origin (*Chem. Trade J.*, 1921, p. 504).

The Manufacture of Nitric Acid from Chile Nitre.

The principle of the manufacture of nitric acid from sodium nitrate by the Retort Process is, briefly, as follows: A charge of about equal weights of dried Chile nitre and concentrated sulphuric acid is heated uniformly in a large cast-iron pot, or "retort" (Fig. 4) provided with a manhole for charging, an outlet pipe above for nitric acid vapour, and a run-off pipe below,

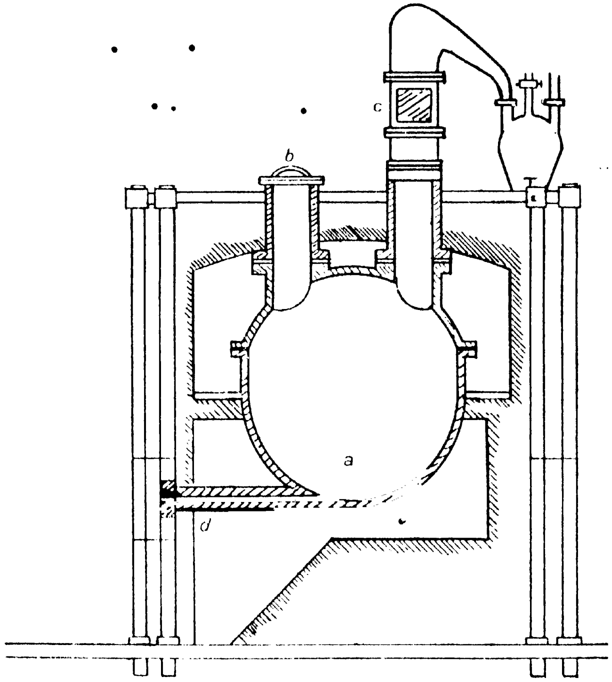


Fig. 4.—Nitric Acid Retort.

a, Body of retort, containing charge; *b*, charging manhole; *c*, exit for vapour of acid, with glass "lantern" for observation; *d*, run-off pipe for fused nitre cake after distillation.

which is plugged during the distillation, from which the fused residue of "nitre cake" in the retort is discharged after the expulsion of acid is complete. The chemical reaction is as follows:

$$(1)\ \underset{\substack{\text{sodium}\\ \text{nitrate}}}{NaNO_3} + \underset{\substack{\text{sulphuric}\\ \text{acid}}}{H_2SO_4} = \underset{\substack{\text{sodium}\\ \text{bisulphate}}}{NaHSO_4} + \underset{\substack{\text{nitric}\\ \text{acid}}}{HNO_3}$$

$$(2)\ NaNO_3 + NaHSO_4 = \underset{\substack{\text{sodium}\\ \text{sulphate}}}{Na_2SO_4} + HNO_3$$

As sodium sulphate is not very fusible, and as the second reaction is complete only at high temperatures, when much of the nitric acid is decomposed, it is usual in practice to aim at producing about equimolecular proportions of sodium sulphate and bisulphate, known as nitre cake.

The nitric acid vapours from the retort are condensed by cooling. Many types of condensing apparatus are in use. Stoneware or "vitreosil" coils, or Woulfe's bottles (Fig. 5), are used, but are fragile and expensive. Another type is the Hart condenser, consisting of a number of horizontal tubes between two vertical "headers"; the vapour passes through the tubes, which are cooled externally by water (Fig. 6).

Some of the nitric acid is always decomposed by the heat into oxides of nitrogen, forming red fumes. These are mixed with air, and condensed to weak nitric acid in absorption towers placed after the condensers (Fig. 5). These towers are packed with pottery balls or other filling, and water is circulated over the packing.

Decomposition is minimised in the Valentiner apparatus (Fig. 9), in which the distillation is carried out at a lower temperature under reduced pressure (see W. Mason, *Chem. Trade J.*, 1921, vol. 69, p. 717).

The following details refer to the process employed at H.M. Explosives Works, Gretna, during 1919.* The sodium nitrate was heated with sulphuric acid in iron retorts by means of producer gas, the nitric acid being distilled off, condensed, and collected, leaving a residue of nitre cake, a mixture or compound of sodium sulphate, Na_2SO_4, and bisulphate, aHSO$_4$. This was ultimately run out of the retorts and ollected. Nitre stocks were brought into sheds by railway

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* Worden, "Technology of Cellulose Esters," vol. i., part 2. London, 1921.

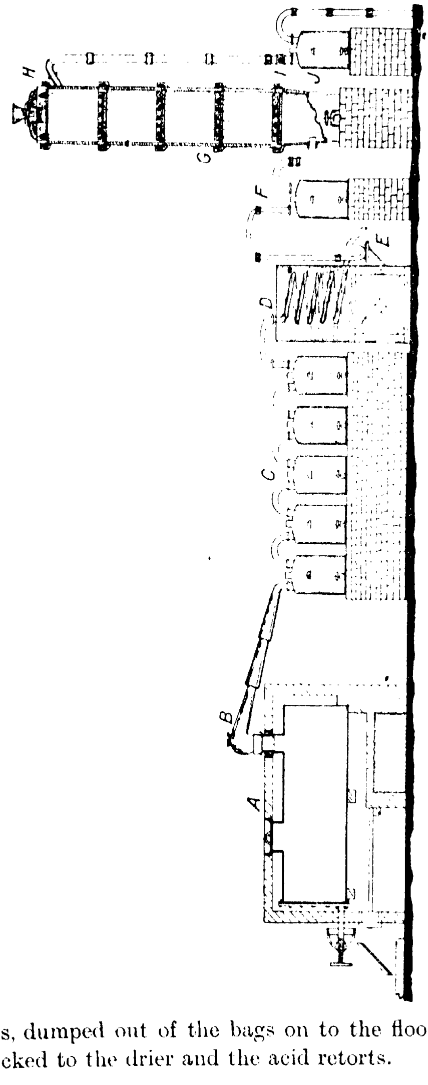

FIG. 5.—SMALL NITRIC ACID PLANT.

A, Horizontal retort; B, vapour exit; C, Woulfe's bottles; D, stoneware or vitreosil cooling coil; E, acid exit; F, Woulfe's bottle; G, tower for absorption of nitrous fumes; H, distributing plate; I, lantern; J, Woulfe's bottle with lime to absorb waste gases.

ars, dumped out of the bags on to the floor of the shed, and rucked to the drier and the acid retorts.

Two driers were provided for the nitrate before use in the retorts, driven by two 20-h.p. motors. The wet nitre was crushed between two rollers set 1 inch apart. A bucket elevator delivered the wet nitre into a Cummer drier, consisting of an inclined revolving cylinder fixed in the flue of a coke furnace. The wet nitrate was fed into the higher end, and, owing to the inclination and rotary motion of the drier, was carried through the hot cylinder in a direction opposite to that of the hot gases. The dried nitre was delivered from the drum by a bucket elevator to a storage bin having a capacity of 150 tons. The bottom of the storage bin, fitted

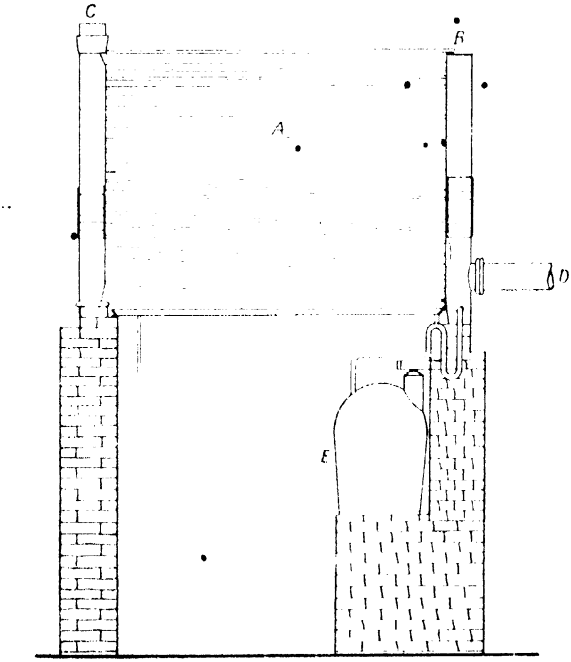

FIG. 6.—HART'S CONDENSER.

B, *C*, Vertical "headers" into perforations, in which are fitted: *A*, the condenser tubes of glass (or other material); *E*, acid receiver; *D*, inlet for acid vapour to be condensed.

with six discharge chutes 1 foot square, delivered the nitre into bogies, passing over a weighbridge, and the contents adjusted to 10 cwt. dry nitre per wagon. This was taken to the retort house and raised by means of an electric lift

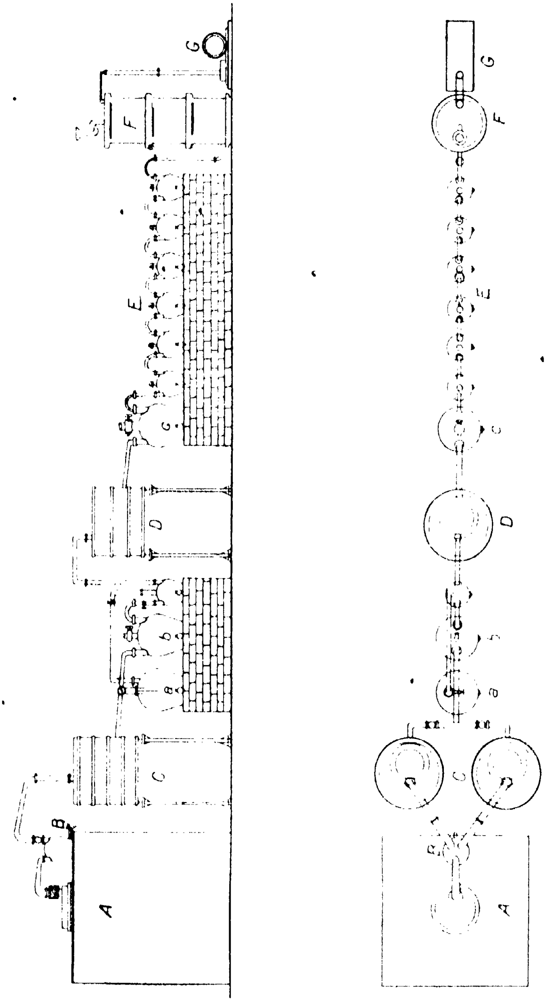

FIG. 7.—VALENTINER NITRIC ACID PLANT FOR CARRYING OUT THE DISTILLATION UNDER PARTIAL VACUUM. *A*, Retort; *B*, spray-catcher; *C*, cooling worm; *a*, *b*, receivers; *D*, second cooling worm; *E*, receivers; *F*, absorption tower for nitrous fumes; *G*, vacuum pump.

to the retort-charging platform. Two 9 feet by 30 feet boiler tanks, elevated on brick piers, were provided for storing sulphuric acid. From these tanks the acid flowed by gravity into the retort house and communicated with the sulphuric acid feed tanks, one of which was allotted to each retort. The retorts, built in sets of three, were gas fired from the side nearest the condensers and tapped from the opposite side. They were completely enclosed in brickwork, excepting the charging lid. Immediately behind the retorts, and about 1 foot above the brickwork top, was a steel-plate charging platform carrying the bogie tracks from the lifts from which the cars of nitre were conveyed to the retorts. The retort, of cast iron, consisted of a lower portion, cylindrical in shape, with a rounded bottom, and a cylindrical extension ring 36 inches high, the two parts being joined by a rust joint. The lid was very slightly dome shaped, and fitted into a collar in the extension ring, connection being made by means of a rust joint. The lid had a large hole about 2 feet 8 inches diameter, to which was bolted, by means of fifteen 1 inch bolts, the iron casting which embodied the charging manhole, which is closed by a lid, and the 8-inch diameter circular hole into which fitted the uptake to the condensing system. The total capacity of the retort was about 9½ tons of water. This size was suitable for the decomposition of 2 tons of nitre. At the lowest end of the retort was a 2 inch outlet for the fused nitre cake.

The condenser platform consisted of an upper and lower deck, the upper deck serving to support the condensers and the fume main, and the lower deck to carry the acid mains. The condenser deck was built of wood or of steel and acid-resisting brickwork. The receiver platform was supported on acid-resisting brick piers. The uptake from the retort was of 8-inch acid-resisting Narki metal (an alloy of iron with about 15 per cent. of silicon), and carried up vertically about 4 feet before bending over to connect with the cascade, which was sloped down at an angle of 80 degrees with the vertical. The cascade was built of straight pipes of Ceratherm, an improvement on pottery ware. The fume passed from the cascade through a bend into Woulfe's bottles, the first of

40 gallons capacity, the second of 15 gallons capacity. From this bottle the fumes passed into the first headers of the first two Hart condensers arranged in parallel. Each of these sets consisted of twenty-six tubes, 6 feet 6 inches long by 1¼ inches diameter. The tubes were sloped, so that any condensed acid ran back to the smaller bottle. Any uncondensed fume passed from the top of the rear headers into a third Woulfe's bottle of 10 gallons capacity, thence into a third Hart unit. In this unit the gases were drawn up from the third bottle through one-half of the tubes, which sloped in the same way as the other two sets of tubes. Any acid condensing there fell back into the 10-gallon bottle, thence to the strong main. From the lower set of fifteen tubes fumes passed to the upper set of eleven, which sloped in the opposite direction. Any gases escaping condensation travelled into the fume main, which connected to the tower system. The condenser tubes were covered with sponge cloths, which distributed water evenly over the surface of the tubes. About 2,000 gallons of water were run down a set of tubes per charge. The surface area of the glass condensing system (three sets) was 159 square feet. The average loss of acid was 10 pounds per house per day.

The acid mains, 3 inches in diameter, built of 2 feet to 2 feet 6 inch lengths of earthenware pipe, ran the entire length of the house, supported on brick arches on a platform below the condensers. Each condensing set delivered into the mains by branch pipes. The strong acid main connected with a 3-inch earthenware pipe at the back of the strong receivers, with branches to three 2-inch lead cooling coils. The weak acid continued along the platform and outside the house to the weak receivers. Eight branch pipes with suitable earthenware cocks connected to eight receivers, reserved for weak acid.

The concentrated acid receivers were built of 20 pound lead in the shape of cylinders, 8 feet 3 inches diameter and 30 inches deep, each receiver having a capacity of about 6 tons of strong nitric acid. A man-lid and a 4-inch dipping hole were provided in the top of each receiver, the former being permanently bolted on, while the latter was covered by a lid fitting into a lute containing a little vaseline. The outlets from the receivers were 2-inch earthenware cocks, connected with a 4-inch lead main to the mixing station.

Ten receivers were provided for weak acid, two reserved exclusively for tower acid. They were of earthenware, of 100 gallons capacity, and of cylindrical shape. The lid was separate and jointed with asbestos jointing.

The exit from the third Hart unit of each condenser set connected with a large 8-inch earthenware fume main which passed along each house. A main of the same size branched off to the absorption towers from the middle of each house. To the first main was connected a smaller 6-inch main which served to exhaust the receivers by means of branches. The fume main was built on a slight slope, so that any condensed acid ran to the lowest point, where it was drawn off to receivers.

The 8-inch earthenware mains were carried outside the houses on wood trestles to the absorption towers, there being two sets, each of eight towers, one set being connected to each house. The towers were elevated on brick piers 12 feet high. The towers were of stoneware, and constructed in five circular sections, each 3 feet long by 3 feet diameter. The column of five sections rested on an earthenware saucer 9 inches deep, having an internal diameter of 3 feet 6 inches. The bottom section had a 9 inch side pipe to connect the gas inlet to the fume main. The towers were packed with graded quartz, resting on a tiled archway built in the saucer to give easy access for the fumes. The size of the quartz packing varied from 6 inches at the bottom to 2 inches at the top. At each section of the joints there was a 2-inch perforated plate with 1-inch holes. The saucer at the foot of the tower was fitted with a 1 inch cock which delivered the weak acid into a constant level receiver situated just below. At the top of each tower was an earthenware acid-distributing bottle known as a "beehive," fitted with four $\frac{3}{4}$-inch bib cocks. Two of these delivered acid from the beehive down the tower. The other two enabled acid to be forwarded from one tower to another through 1-inch glass pipes.

Pohle air lifts or acid elevators were used for lifting the acid from the constant level receivers to the tops of the towers. The gases conveyed along the fume main entered at the foot of No. 1 tower, were drawn through the tower, they left by an 8-inch ∩ bend, and were conveyed to the bottom of the second tower, and so on through the series. The absorption was carried out by counter-circulation of absorbing liquid (water or weak nitric acid) and the nitrous fumes. Air at 15 pounds per square inch pressure was supplied to the glass air tube, and a continuous but jerky lift of acid to the beehive on the top of the tower maintained. The compressed air served two purposes, viz., to elevate the acid from the bottom to the top of the tower, and also to oxidise the NO passing through the towers to NO_2, which in contact with H_2O and air forms HNO_3: $2NO_2 + H_2O + O = 2HNO_3$.

A 30-inch diameter fan, driven by a 10-h.p. motor, caused a blast of air to be driven through an earthenware injector. The suction pipe, also of earthenware, communicated with the gas outlet from No. 8 tower. By this means a vacuum of 6 inches water gauge was produced on No. 8 tower, and drew the gases through the system of towers.

Labour Requirements for two adjoining retort houses, each containing twenty-four retorts:

Female Labour (nitrate of soda handling): Sixteen girls per shift engaged as under: 1 charge-hand; 3 girls picking down nitre; 6 girls filling bogies and conveying same to the drier; 3 girls feeding driers (1 spare); 2 girls conveying nitre from dry bins to hoists; 1 girl checking weights of dry nitre.

In addition to above girl truckers, 2 dip or receiver girls per shift were employed as process workers.

Total female labour per shift; 18 per house; total for day, 54 girls.

Male Labour: One foreman per shift; 21 operatives per shift.

The various process operatives were classified, and the men carefully selected for their respective jobs. The senior process man was the reaction man responsible for a series of twelve retorts and his duties were—

(1) Running the charge of sulphuric acid into the retort.
(2) Controlling the distillation.
(3) Attending to gravities of the nitric acid.
(4) Seeing that his section was kept clean and tidy.
(5) Controlling condensers (cloths and water), but not the replacing of broken tubes.

Tapping Retorts: Two men provided in each house, their work being to empty the retort of its nitre cake. They were responsible for all plugs being properly secured before the acid was run into the retort.

Charging Men: Two provided; their work consisted of bringing the nitre along to the retort mouth, emptying it into the retort, cementing up the lid, and generally cleaning up the retort top.

Condenser Men: Two men engaged attending to condensers generally, replacing broken tubes, and patching and overhauling condenser standards and joints.

Granulating Nitre Cake: Two men per shift required.

Nitre Drier: One man per shift required for driers, who also attended to tarring and greasing of all bogies

Lump Cake: Three men engaged on the removal of lump nitre cake to the wagons which ran alongside the pans. One senior charge-hand provided for each shift.

Summary of Male Process Labour: One senior charge-hand; 4 reaction men; 4 tappers; 4 charging men; 1 man in charge of nitre drier; 5 men disposal of nitre cake; 2 condenser men; total, 21 men per shift. The foreman was generally responsible for the running of the plant and control of the labour.

Maintenance of Labour: The wear and tear on a plant of this kind is naturally great. A gang of earthenware pipe jointers was engaged on the nitric acid subsection. Fitters were also available for engineering troubles, and also plumbers, but none were permanently on the retort staff.

Attached Labour: The fires were controlled, under the orders of the reaction man, by a man supplied by the producer plant. Two firemen per shift were provided for the two retort houses. Another man belonging to the acid-mixing station supplied the sulphuric acid for the two retort houses.

Plant Operation—Sampling of Nitre: The crude nitre was sampled weekly. When sampling, about 20 cwt. were generally taken down, halved and quartered in the usual way until 28 pounds were obtained. The following is the average analysis of the sodium nitrate:

	Per Cent.	
Sodium nitrate	95·85	} — Sodium nitrate 96·6 per cent.
Potassium nitrate	0·98	
Potassium perchlorate	0·14	
Sodium chloride and sulphate	0·50	
Insoluble	0·06	
Moisture	2·20	
Iodates	Trace	

This was usually dried so that the finished sample contained 0·5 per cent. moisture, this usually bringing the nitrate content of the sample to 98 per cent.

Usage of Sulphuric Acid: In each retort 2 tons of nitre were distilled with approximately 2 tons of 92 per cent. sulphuric acid. The following are the actual figures:

2 tons nitre at 98 per cent.	1·96 tons pure $NaNO_3$.
1 inch dip in tank	0·059 ton.
34·5 inches used	34·5 × 0·059 = 2·035 @ 92 per cent.
	1·872 H_2SO_4 (2 tons C.O.V. of 92 per cent.).

Ratio of sulphuric acid to nitrate in terms of pure chemicals:

$$\frac{H_2SO_4}{NaNO_3} = \frac{1{\cdot}872}{1{\cdot}960} = \frac{0{\cdot}956}{1{\cdot}000}.$$

The following are average producer gas and waste flue gas analyses:

	Producer Gas.
CO_2	4·0
CO	28·0
H_2	11·1
CH_4	1·4
N_2	55·5
Total	100·0

	Waste Fuel Gas.
CO_2	8·1
O_2	9·9
N_2	82·0
Total	100·0

Experiments were made under varying conditions to determine exactly the coal consumption. The average figure recorded was 30,000 cubic feet of gas reduced to normal temperature, for a charge of 2 tons of nitre, which gives 1·43 tons HNO_3.

1 ton of coal gives 130,000 cubic feet of gas.
(1·43) 1 charge uses 30,000 cubic feet of gas.
Hence 1 ton uses 20,000 cubic feet of gas,
equivalent to 0·14 ton fuel per ton HNO_3.

After the acid had been added and the plug luted down, the fire was started, unless the retort was very hot, in which case it was advisable to wait for a short time. Sufficient fire was put on to make distillation commence in about one hour. If the retort be cold much longer will be required – up to three or four hours.

For ordinary running a fourteen to sixteen hour cycle was the most usual, with a distillation time of twelve to fourteen hours. As soon as a retort was warm, a little brown fume appeared in the condenser tubes.

When the "pot" reached a temperature of 115° to 120° C. the reaction between the sodium nitrate and the sulphuric acid became violent.* The pressure in the retort rose. At this stage it was usual to draw the fire while the violent reaction was in progress, to avoid damage to the pottery. This reaction lasted from five to twenty minutes, depending largely on the speed with which the pot temperature had been raised.

From now onwards the specific gravity (sp. gr.) of the liquid distilling was taken every hour by the "reaction man." When the sp. gr. of the distillate fell to 1·465 the acid made was run to the weak acid receivers; till this point it had been running into the strong receivers. The distillation was now steadily continued till the sp. gr. of the distillate reached 1·340; then the fire was extinguished, and there was sufficient heat in the charge to finish the distillation while preparations were made for tapping.

During the process of distillation the bulk of the acid was condensed in the first two headers of Hart tubes. A small quantity condensed in the third set of tubes and this usually contained upwards of 5 per cent. of nitrous acid. Uncondensed gases passed to the fume main and to the absorption towers.

Absorption of Nitrous Fumes from Condensers. Cold water was fed into No. 8 tower (nearest the exhaust), and the ¾-inch cocks on the beehive so adjusted as to give a progressive movement of acid through the system. Acid of between 60 and 65 per cent. strength ran off at No. 1 tower, and was conveyed to the storage by means of a 2 inch pipe.

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* See Webb, *J. S. C. I.*, 1921, 212 *T.*

Capacity of Plant.—Assuming twelve hours as the lowest cycle consistent with efficient condensation and few breakages, we have 1·40 tons HNO_3 from a charge in twelve hours. Allowing two hours dead time, the balance of the working day of twenty-four hours will give 1·16 tons nitric acid.

∴ 1·4 + 1·16 = 2·56 tons HNO_3 per retort per twenty-four hours.

Each house contains twenty-four units, two of which were generally being repaired:

$$24 - 2 = 22 \times 2 = 44 \times 2{\cdot}56 = 115 \text{ tons } HNO_3 \text{ per day.}$$

The quantity of $NaNO_3$ used per ton HNO_3 produced was about 1·39 tons.

The following was an average percentage return for nitric acid:

Recovered as strong acid, 87·2 (strength, 92·5 per cent. HNO_3).
Recovered as weak acid (*ex* towers), 10·4 (strength, 63·5 per cent. HNO_3).
Recovered as tower acid weak, 2·4 (strength, 56·5 per cent. HNO_3).

Nitric Acid Retorts (North and South Houses), Monthly Report.

Five weeks ended 7.30 a.m., March 2, 1918.
All weights in tons of 2,240 pounds.
Total number of retorts charged, 138½ wet, 1,359½ dry = 1,498.
Total number of retorts tapped, 1505

Sodium Nitrate:	Charged:
Amount wet, 276·5 tons.	$NaNO_3$ 96·6 per cent. as HNO_3, 197·97 tons.
Amount dry, 2719·5 tons.	$NaNO_3$ 98·41 per cent. as HNO_3, 1983·58 tons.
Sulphuric Acid:	
Amount, 3095·52 tons.	H_2SO_4 92 per cent. as H_2SO_4, 2849·44 tons.
Coal used in producers, 401·54 tons.	

Nitric Acid Produced:

Amount strong, 1986·07 tons as HNO_3 92·4 per cent.; as HNO_3	1835·62 tons.
Amount weak, 380·19 tons as HNO_3 63·75 per cent.; as HNO_3	242·38 ,,
Ex towers, 106·67 tons as HNO_3 59·7 per cent.; as HNO_3 ..	63·67 ,,
Total ..	2141·67 ,,

Total HNO_3 charged to plant as $NaNO_3$	2181·55 tons.
Total HNO_3 recovered	2141·67 ,,
Unaccounted for at mixers	20·71 ,,
Total amount lost	60·59 ,, (2·78 per cent.).
Time of distillation	11 hours 43 minutes.
Time of cycle	14 hours 48 minutes.

Nitre Cake:

Percentage free H_2SO_4: 28·43 per cent. by analysis, 31·45 per cent. by calculation.

Fuel:

Coal used per ton of acid recovered	0·16 ton.
Coal used per ton of HNO_3	0·19 ,,

Nitric Acid:

Average strength of acid recovered	86·6 per cent.
Tons produced per retort	1·6
Percentage recovered as strong acid	85·7 per cent.
Percentage recovered as weak acid	11·3 ,,
Percentage of weak acid recovered in towers	3·0 ,,
Total recovery	97·22 ,,

The Chile Nitrate Industry.

Before the war practically the whole of the world's requirements in respect of combined nitrogen in the form of nitrate were met by the exportation of sodium nitrate from Chile, and the price of this product has hitherto governed the market price of combined nitrogen.

The Chilean nitrate industry is of about a century's standing, and has been characterised by a steady rate of expansion. By the middle of the nineteenth century the exports had attained a figure of about 100,000 tons per annum, whereas the shipments from Chile in the year prior to the war (1913) amounted to over 2,400,000 tons.

Output and Market Prices.

Exportation from Chile may be said to have commenced in 1830. The following export figures are given by Newton (*J. S. C. I.*, 1900, 408), covering the first seventy years:

Year.	*Tons Exported.*	*Price per Ton in March.*
		£ s. d.
1830	8,348	28 0 0 (1832)
1835	—	21 0 0
1840	10,500	20 10 0
1850	22,870	15 0 0
1860	61,171	15 10 0
1870	131,402	16 10 0
1880	111,120	*19 0 0
1885	482,030	9 10 0
1890	1,003,340	8 5 0
1895	...	9 0 0
1899	1,355,360	8 5 0

In 1879 an export duty of about seventeen shillings per long ton was imposed by the Chilean Government. The following year this was raised to three times that amount, and has remained at that figure ever since.

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* War between Chile and Peru.

The scale of production during the years 1903 to 1919 and the corresponding average annual market prices of nitrate in the United Kingdom are set out in the table below.

Prices became irregular and merely nominal at the beginning of December, 1915, and remained so until about February, 1919. By January, 1921, freights for Chile nitrate to the United Kingdom had dropped from the war figure of £10 per ton to £3 5s. per ton, but the price of the product in England was maintained at the high average of £22 14s. for January, 1921. In January, 1922, the price had fallen to £14 5s. per ton, f.o.b. Liverpool, for 96 per cent. refined nitrate.

OUTPUT OF CHILE NITRATE.

Year.	*Production.*		*Average Annual Market Prices in United Kingdom, ex-ship Liverpool.*				*Average Price f.o.b. Chile, Year ending June 30.*	
	*Nitrate.**	*Combined Nitrogen on Basis of 15·65 per Cent. Nitrogen (= 95 per Cent. Nitrate).*	*Nitrate, 95 per Cent. (= 15·65 per Cent. Nitrogen) in Liverpool, per Long Ton.*			*Combined Nitrogen, per Metric Ton.*	*Nitrate (95 per Cent.), per Long Ton.*	*Combined Nitrogen, per Metric Ton.*
	Long Tons.	*Metric Tons.*	£	s.	d.	£	£	£
1903	1,429,150	227,230	9	10	10	60·01	—	—
1904	1,421,580	226,030	10	4	2	64·20	—	—
1905	1,543,120	245,350	10	16	10	68·19	—	—
1906	1,639,300	260,640	11	6	8	71·28	—	—
1907	1,646,890	261,850	11	3	4	70·23	—	—
1908	1,733,540	275,630	10	4	2	64·20	—	—
1909	1,922,000	305,590	9	15	0	61·32	—	—
1910	2,251,000	357,900	9	7	6	58·96	—	—
1911	2,313,450	367,830	9	17	11	62·24	—	—
1912	2,485,860	395,250	11	1	8	69·70	—	—
1913	2,464,540	391,860	11	1	8	69·70	—	—
1914	2,432,328	386,250	10	8	9	65·5	8·56	54·0
1915	1,734,932	275,510	12	13	0	79·60	6·99	44·0
1916	2,877,899	457,010	17	12	5	111·00	8·45	53·2
1917	2,966,061	471,010	25	5	0	159·00	10·0	63·0
1918	2,831,026	449,567	26	6	6	165·4	13·12	82·6
1919	1,658,826	266,187	21	2	9	131·3	13·3	82·9
1920 (1st half)	1,182,000	190,283	24	18	8	154·8	17·5	108·8
1920 (2nd half)	—	—	23	17	0	148·5	—	—

* Figures supplied by the Chilean Nitrate Committee.

World's Consumption of Chile Nitrate.

The following figures have been given for the total consumption of Chile nitrate in different countries during 1911, 1912, and 1913:

WORLD'S CONSUMPTION OF CHILE NITRATE.

Country.	*Quantities in Metric Tons.*		
	1911.	1912.	1913.
Germany	743,412	911,962	833,112
United States	568,136	441,047	589,187
France	338,706	354,517	327,192
Belgium	303,780	309,817	318,515
Holland	141,652	180,924	164,502
United Kingdom	132,931	137,415	128,561
Italy	53,616	44,545	51,690
Egypt	19,018	23,981	25,638
Spain	8,977	13,554	13,150
Austria-Hungary	5,281	7,114	7,445
Denmark	3,438	4,825	10,748
Switzerland	2,371	5,198	-
Other Countries	77,074	95,746	87,233
Total	2,401,392	2,530,645	2,556,973

Statistics from "Production et Consommation des Engrais Chimiques dans le Monde," Institut International d'Agriculture, Rome, 1920; also monthly *Bulletin of Agricultural Intelligence and Plant Diseases*, International Institute of Agriculture, Rome, Year 5, No. 9, September, 1914.

From 70 to 80 per cent. of the total consumption of Chile nitrate was therefore accounted for by the requirements of Germany, the United States, France, and Belgium alone.

War Influences.

Great developments in the Chile nitrate industry were brought about by the war demand, and on account of the isolation of Germany and her allies from overseas supplies, a striking readjustment as regards the principal consumers of Chile saltpetre took place during the war period.

The statistics are necessarily incomplete, and are to be regarded only as a fair approximation. The following table gives information relative to the production, consumption, exports, deliveries, stocks, etc., of Chile nitrate during the period 1913 to 1919.

The production in 1917 and 1918 was higher than any previously recorded, and it is apparent that the loss of the German market was more than counterbalanced by the war demand of the Allies and the requirements of other countries. On the other hand, there was an increasing accumulation of stocks on the Chilean coast, the shipments to the American and European markets having been hampered by the lack of tonnage and the great increase in the cost of freight.

World's Consumption of Chile Nitrate during the War Period (1914–1919) in Metric Tons.

Country.	1914.	1915.	1916.	1917.	1918.	1919.
Germany.. ..	589,854*	—	—	—	—	—
U.S.A.	550,408	704,581	1,237,975	1,567,977	1,673,823	369,641
France	297,180	254,008	540,700	453,664	256,572	156,169
Belgium	158,482*				—	79,269
Holland	149,807	50,857	60,877	55,801	1,128	151,301
United Kingdom	357,281	368,929	414,694	247,189	534,700	24,878
Italy	59,850	71,730	85,649	104,150	97,012	12,868
Egypt	52,325	53,076	19,350	32,662	2,888	54,468
Spain	36,082	38,376	44,731	52,324	18,751	58,230‡
Denmark.. ..	42,592	12,058	34,948	39,600	116	48,108
Switzerland ..	2,280	199	343	259	541	1,078
Norway	560	34	6,426	45	7	—
Sweden	41,657	33,908	36,360	17,179	6,763	23,212
Russia	53,982	34,120	33,121	213†	—	..
Japan	24,425	30,211	46,021	55,086	48,906	65,706
Australia.. ..	3,429	3,430	5,700	8,406	2,733	1,955
New Zealand ..	443	827	146	657	207	—
Canada	12,503	20,541	44,990	20,942	47,170	4,121

It is quite clear that the industry will have to reckon with the permanent loss of at least a portion of the German market, owing to the development in that country, under the stress of war necessity, of an important synthetic nitrate business, which is now available for peace-time production. Against this, however, must be set the fact that the position of Chile nitrate as a fertiliser is established and proved, and the

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* Six months. † Seven months. ‡ Eleven months.

CHILE NITRATE.*

Year, April 1 to March 31.	Production.		Exports.		World's Deliveries.		Chile Stocks (March 31).		Average Price f.o.b. Chile (Year ending June 30).		Oficinas Working.
	Nitrate. Long Tons.	*Combined Nitrogen.† Metric Tons.*	*Nitrate. Long Tons.*	*Combined Nitrogen.† Metric Tons.*	*Nitrate. Long Tons.*	*Combined Nitrogen.† Metric Tons.*	*Nitrate. Long Tons.*	*Combined Nitrogen.† Metric Tons.*	*Nitrate per Long Ton.*	*Combined Nitrogen† per Metric Ton.*	
									£	£	
1913–14	2,745,000	436,000	2,695,000	428,500	2,715,000	431,000	511,000	81,200	8·56	54·0	134
1914–15	2,010,000	319,500	1,495,000	237,500	‡	‡	1,010,000	160,500	6·99	44·0	43
1915–16	2,218,000	352,000	2,365,000	376,000	‡	‡	821,000	133,000	8·45	53·2	117
1916–17	2,850,000	453,000	2,880,000	458,000	‡	‡	771,000	122,500	10·0	63·0	121
1917–18	2,970,000	472,000	2,695,000	428,000	‡	‡	1,005,000	159,600	13·12	82·6	124
1918–19	2,600,000	413,000	2,455,000	390,000	‡	‡	1,168,000	185,500	13·3	83·8	116
1919–20	1,713,000	272,000	1,700,000	270,000	‡	‡	1,220,000	194,000	17·5 June approx.	110·0 June approx.	80

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* Authority, "Nitrate Facts and Figures," 1920, A. F. Brodie James.

† Assuming nitrate contains 15·65 per cent. nitrogen.

‡ Dislocation owing to war conditions—figures not available.

only factor which can jeopardise its continued worldwide use is the price at which the product can be marketed, in comparison with synthetic material.

British Imports of Chile Nitrate.

The most essential of all nitrogenous products imported by the United Kingdom is undoubtedly Chile nitrate, and although statistics are not available as to the precise relation between the agricultural and industrial demands, there is no doubt that agriculture claims the major portion, at least in so far as concerns pre-war allocation.

The Chilean Nitrate Committee estimate this fraction as two-thirds of the whole, and other authorities quote 75 per cent. of the world's consumption as being put to agricultural use.

The requirements for industrial purposes are mainly in connection with the manufacture of nitric acid, sulphuric acid, and potassium nitrate. These industries, of course, accounted for the large increase of importation during the war period.

British Importation of Chile Nitrate.

Year.	*Chile Nitrate.*	*As Combined Nitrogen on Basis of a Nitrogen Content of 15·65 per Cent. (= 95 per Cent. Purity).*
	Long Tons.	*Metric Tons.*
1903	116,715	18,550
1904	120,526	19,160
1905	104,436	16,600
1906	108,486	17,250
1907	113,894	18,110
1908	145,724	23,170
1909	90,207	14,340
1910	126,498	20,110
1911	128,487	20,430
1912	123,580	19,650
1913	117,895	18,745
1914	351,631	55,999
1915	416,520	66,227
1916	408,896	65,014
1917	248,190	39,462
1918	526,300	83,682
1919	196,299*	31,211*
1920	99,967	15,895

* Importation, 24,485 tons; war stock sold abroad, 220,784 tons.

The enormous increase during the war period is evident, the total during 1918 amounting to more than four times the average pre-war figure. During the war period most of the Chile nitrate imported was diverted to war purposes. In 1918, for example, the net importation for fertiliser purposes was only 300 tons, as compared with 155,081 tons in 1914. In 1918 the nitrate imported for munition purposes was 534,400 tons, as compared with 202,200 tons in 1914. In 1920, of the total importation of 147.476 tons, 47.509 tons were re-exported. 99.967 tons used for fertiliser and none for munitions. The situation during the war period is summarised in the following table:

Year.	*Total Imports.*	*Used for Fertiliser*	*Consumed or Allocated to Stock for War Purposes.*	*Re-exported.*
1913	128,561	--	--	10,666
1914	370,910	171,874		19,279
1915	458,964	131,520	285,000	53,441
1916	409,621	20,896	388,000	725
1917	253,032	1,190	247,000	4,842
1918	526,305	300	526,000	5
1919	24,485	24,452		220,784
1920	147,476	99,967	--	47,509

Those who are interested in discovering a definite policy of the Government during the war period with regard to the requirements of munitions and food (fertilisers) may find this table instructive. In connection with fertiliser requirements it must be noted that the production of ammonium sulphate, the only alternative nitrogen fertiliser, during the war period, showed a considerable decline as compared with the production in 1913 (see p. 123).

*The Economics of the Nitrate Industry.**

The two most important aspects of the Chilean nitrate industry from an economic standpoint are those relating to (1) the period during which the deposits will repay exploitation, and (2) costs of production and marketing.

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* See Final Report of the Nitrogen Products Committee, 1920.

1. *Life of the Deposits.*

Various estimates have been published from time to time as to the probable life of the caliche deposits in the face of the rapidly increasing demand.

(1) According to a statement published in *The Times* Finance, Commerce, and Shipping Supplement, November 22, 1913, and issued by the Chilean Nitrate Committee, the following facts were given by Señor Francisco J. Castillo, the Inspector-General of the Nitrate Deposits, in an official report presented to the Chilean Government:

(*a*) The zone of nitrate-bearing grounds comprises some 200,000 square kilometres, of which so far only 5,811 square kilometres have been examined by excavations and test holes. The last-named area is owned partly by various companies and firms, and partly remains in the hands of the Chilean Government.

(*b*) The examined area was calculated to contain some 290,300,000 tons of sodium nitrate, of which up to that time 45,000,000 tons had been extracted and exported. The remainder, at the rate of production then existing, was equivalent to a further 100 years' supply.

(*c*) The unexplored area is some thirty-four times larger than the examined grounds, and assuming that the former contains only as much recoverable nitrate of soda as the latter, a further 100 years' supply is thus obtainable.

(*d*) In the examined grounds no raw material containing less than 11 per cent. of sodium nitrate has been taken into consideration, nor grounds where the thickness of the layer of the raw material was less than 1 foot, except in the case of raw material containing at least 25 per cent. of sodium nitrate, when the thickness of 8 inches and above has been included.

The superficial area of each portion of ground examined has been divided by the total number of test holes made, in order to arrive at the area applicable to each test hole, and this consequently determines the total nitrate-bearing area.

From the theoretical quantity of pure sodium nitrate resulting from the above operations, a reduction of 40 per cent. has been made in order to provide for losses in extraction, manufacture, errors of calculation, etc.

(*e*) Of raw material of a lower grade vast quantities remain, which have been excluded from these calculations because they could not then be profitably extracted under the existing system of work; but as improvements are being constantly made there would appear to be reason to assume that even this low-grade material will be worked when the richer qualities are exhausted.

The above estimate was doubtless based upon surveys carried out prior to or early in 1913, and possibly upon the older methods of extraction, which only resulted in the recovery of about 50 per cent. of the nitrate in the material treated. The introduction of improved methods of extraction and treatment, to which reference is made, has been accelerated during the last few years in consequence of the increasing demand for Chile nitrate, and it is considered by good authorities that further developments may eventually lead to the extraction of as much as 85 per cent. of the nitrate. Improvements of this character may add appreciably to the life of the deposits on the basis of the pre-war rate of production.

On the other hand, the statement quoted, unlike Sir William Crookes's estimate prepared in 1898, does not take into account the normal growth of the world's demand, which approximately doubles every ten years. Moreover, it omits all reference to the possibility of a still more rapidly increasing demand in the future. It is also important to note that the deposits are often far from uniform in composition, and extend over very large areas in desert regions remote from the coast. In many cases, therefore, the cost of exploitation would be prohibitive on account of the cost of labour, fuel, and transport, which is continually advancing in Chile, as elsewhere.

(2) According to further authoritative evidence, a more recent report has shown that the life of the explored grounds alone at the present rate of production is of the order of 100 years, without making allowance for the inferior deposits capable of utilisation in the future owing to improvements in the methods of extraction. The average life of the grounds of existing English nitrate companies was stated to be about thirty-seven years.

(3) In other publications issued by the Nitrate Propagan Association it is stated that the explored deposits, on t basis of a minimum content of 10 per cent. of sodium nitra in the mineral treated, contain 200 million metric tons utilisable nitrate—*i.e.*, capable of being extracted at average price (at the deposit) of 3·75 francs (say 3s.) p Spanish quintal.* The country would thus be able to mark 3,000,000 metric tons per annum for a period of seventy yea but if allowance is made, upon the basis of past years, f an annual increase in production of 55,000 metric tons, t explored deposits would last only until 1966 (Abstract, *Month Bulletin of Agricultural Intelligence and Plant Diseases*, Inte national Institute of Agriculture, Rome, Year 8, No. 7, Jul 1917).

There are various considerations entering into the questi of the probable life of the deposits, such as the scale of t future demand for nitrate, the rate of exhaustion of the rich and most accessible deposits, and the less profitable charact of the operations when recourse is had to lower-grade and le accessible deposits. These factors will, in turn, be influenc to a substantial degree by future reduction in the mark price of the product.

To sum up, the evidence available affords every reason f believing that the deposits of the raw material "caliche" a adequate for meeting all demands for perhaps a century more. Their commercial life, as distinguished from th actual capacity, will depend, however, upon the econom factors just mentioned, and it is difficult in consequence form an estimate of the probable duration of the period profitable working.

2. *Production Costs, etc.*

(*a*) *Capital Cost of Nitrate Factory in Chile.*—The price which nitrate property is offered for sale by the Chile Government is based upon the amount of nitrate of so upon the property, and an average purchase price amounts 3d. per quintal.

The pre-war capital cost of a medium-sized modern nitra

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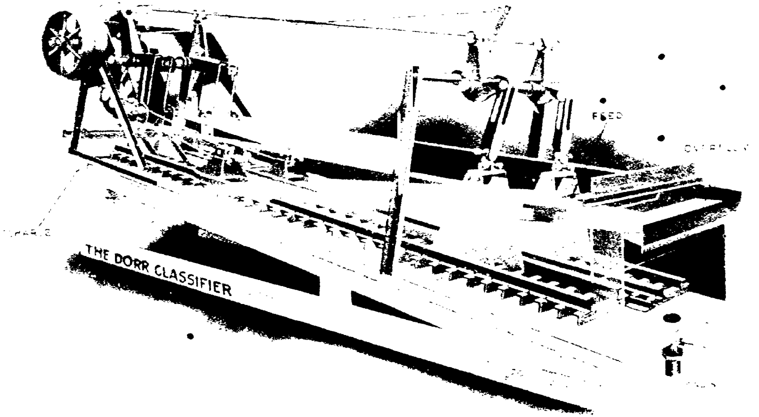
* Twenty-two Spanish quintals = 1 ton of 2,240 pounds.

PLATE IV.



DORR CLASSIFIER

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factory with an average production of, say, 24,000 tons of Chile nitrate per annum, including the purchase of nitrate grounds having a life of about twenty years, would be as follows:

	£
Purchase of nitrate grounds	125,000
Factory with all necessary buildings and plant	150,000
Loose plant, including locomotives, cars, stores, etc.	25,000
Water and railway sidings	25,000
Total	325,000

For an annual output of 24,000 long tons of 95 per cent. nitrate (15·65 per cent. nitrogen) the capital outlay thus amounts to £13·54 per ton of Chile nitrate per annum.

The output of a factory of the size indicated above could be marketed by a steamer carrying 8,000 tons dead weight and making three round voyages per annum. The pre-war cost of such a vessel would amount to £70,000, and if half the capital cost is assigned to home-bound nitrate and the other half to outward-bound cargo, the additional capital involved amounts to £1·46 per long ton of Chile nitrate per annum.

The total capital therefore involved in nitrate plant and in shipping for marketing the product in Europe amounts to £15 per long ton of Chile nitrate per annum.

(*b*) *Cost of Production.*—There are two grades of material placed upon the market—

(1) That containing not less than 96 per cent. of sodium nitrate (over 16 per cent. nitrogen) used in chemical industry.

(2) That containing 95 per cent. of nitrate (not less than 15·5 per cent. nitrogen) used for fertiliser purposes.

Imported sodium nitrate is very uniform in composition, and generally contains 1 to 2 per cent. of sodium chloride.

According to authoritative data supplied to the Nitrogen Products Committee (see Final Report, 1920, from which the following figures are taken), the pre-war cost of production at a medium-sized modern nitrate factory, including all factory expenses in Chile—such as labour, fuel, repairs, bagging, freight to a port, shipping charges, and commission, amortisation of the cost of the nitrate grounds and plant, interest on capital at the rate of 5 per cent., and Chilean export duty at 2s. 4d. per Spanish quintal (101·8 pounds)—amounted to 7s. 4d. per quintal of nitrate f.o.b. in Chile, or £8 1s. 4d. (£8·07) per long ton of nitrate (95 per cent. purity). The expenses incurred in marketing the product in Europe, including sea freight at 25s. per ton, loss in weight during the voyage, landing charges, and port dues, increased the cost to about £10·2 per long ton on shore in England. These figures for the pre-war cost of production per ton of nitrate (95 per cent. purity, containing 15·65 per cent. nitrogen) are summarised below.

CHILE NITRATE (15·65 PER CENT. NITROGEN).

	Per Long Ton.	*Per Metric Ton.*
	£ s. d.	£ s. d.
All factory expenses in Chile, including labour, fuel, repairs, sundries, bags and bagging, freight to port, shipping charges, and commission (4s. per quintal)	4 8 0	4·330
Amortisation of grounds, and depreciation and interest on plant (1s. per quintal)	1 2 0	1·082
	5 10 0	5·412
Sea freight (25s.) and insurance (2s. 6d. per ton)	1 7 6	1·353
	6 17 6	6·765
Loss in weight during voyage, landing charges, and port dues (average)	0 15 0	0·738
Chilean export duty (2s. 4d. per quintal) ..	2 11 4	2·525
Cost on shore, England or Continent	10 3 10	10·028

The pre-war market price (average 1911–1913) of Chile nitrate in this country amounted to £10 13s. 9d. (£10·69) per long ton. There are considerable variations in the production costs at different nitrate factories, and the average cost for the whole industry under pre-war conditions, inclusive of all expenses and export duty, may be taken at about 6s. 6d. per quintal f.o.b. in Chile. Upon this basis the total cost on shore in England would thus have been about £9·27 per long ton.

During the war period the selling price of Chile nitrate in the United Kingdom increased substantially (see table on p. 66). That the transport situation was largely the cause of this is seen from the following table, which gives the average value of the material at a Chilean port, excluding export duty, ocean freight, insurance, commission, etc. It will be noted that, while some increase is apparent during the war period, this is not wholly abnormal.

Year.	*Average Value (Pounds per Long Ton) at Chilean Port.*	*Year.*	*Average Value (Pounds per Long Ton) at Chilean Port.*	*Year.*	*Average Value (Pounds per Long Ton) at Chilean Port.*
1867	8·80	1885	7·14	1903	6·30
1868	7·06	1886	7·67	1904	6·48
1869	9·57	1887	6·99	1905	7·05
1870	11·10	1888	6·30	1906	7·21
1871	11·72	1889	6·93	1907	8·44
1872	11·96	1890	6·10	1908	7·82
1873	11·30	1891	6·13	1909	7·33
1874	9·92	1892	5·80	1910	6·30
1875	8·54	1893	6·75	1911	6·44
1876	9·39	1894	6·50	1912	6·58
1877	11·20	1895	6·79	1913	7·24
1878	10·61	1896	6·24	1914	6·55
1879	8·13	1897	6·52	1915	5·82
1880	12·38	1898	4·48	1916	6·15
1881	11·02	1899	3·46	1917	7·20
1882	9·76	1900	5·28	1918	8·96
1883	8·39	1901	5·84	1919	10·40
1884	7·55	1902	5·94		

(*c*) *Future Market Price.*—The price at which Chile nitrate can be marketed at any spot remote from Chile is governed by the following items:

(i.) The cost of extraction, including all stages of manufacture, such as blasting, crushing, lixiviation, crystallisation, etc., and overhead charges.
(ii.) Materials, such as fuel, water, and bags.
(iii.) Labour charges, including packing.
(iv.) Transport to port.
(v.) Export duty levied by the Chilean Government.
(vi.) Freights.
(vii.) Commissions and insurance.

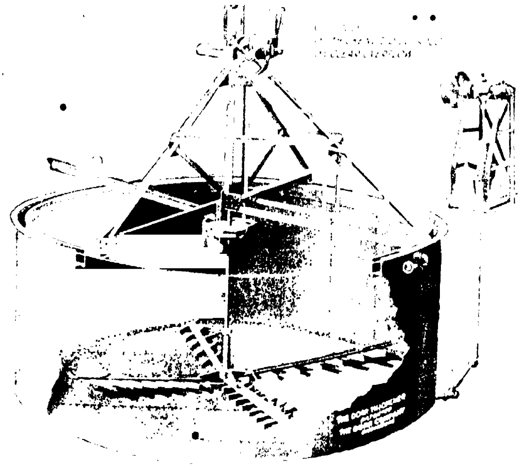
The only items which may be regarded as of minor importance are (iv.) and (vii.), and an alteration in any one of the others may have a substantial influence upon the price at which the material is finally delivered to the consumer.

Cost of Extraction.—Research carried out and experience gained during the last few years seem to indicate that the cost of extraction may in the future be considerably reduced, principally by the use of better-designed plant, enabling poor-grade raw material to be more efficiently worked. It has been estimated that 9d. per quintal, or 16s. 6d. per ton, might reasonably be saved in this regard.

Materials and Labour.—It is difficult to form any reasoned estimate as to the future tendencies as regards these items of cost. The effect of the war, in Chile as elsewhere, was to occasion considerable all-round advances, amounting in all to several shillings per quintal of product. It is doubtful whether these charges will ever again fall to the pre-war level, and some authorities even express the opinion that further increase is to be looked for.

Export Duty.—The duty levied upon the export of nitrate has in the past formed the main source of revenue of the Chilean Government. The threatened loss of the market, however, such as by the competition of synthetic products or otherwise, might under certain circumstances cause the authorities to reduce the present charge of some 51s. per ton. Authoritative information given to the Nitrogen Products Committee indicates that upon the basis of a reduction of 50 per cent. in the duty improved methods of extraction would enable the nitrate to be produced for 4s. 3d. per quintal f.o.b. in Chile, and that with freights at their pre-war level the product could be marketed in Europe for £8 per long ton. Other estimates lead to the conclusion that if the greatest possible reductions were taken at 9d. per quintal in the cost of extraction, 80 per cent. decrease in export duty, and 5s. per ton off the pre-war freight rates, this figure might be reduced to £7 per long ton, as representing the lowest possible market price in England or on the Continent. This would provide no profit for the producer, but would allow of 5 per cent. interest on the capital value of the nitrate plant. These

PLATE V



DORR THICKENER.

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figures must be regarded as entirely problematical, and their realisation would indicate a last effort on the part of the industry to maintain its position.

Combined Nitrogen in Agriculture.

Many nitrogenous substances, more particularly nitrates and ammonium sults, are used as plant manures. The natural formation of combined nitrogen is insufficient to supply the soil, more particularly on account of the wastage through the action of denitrifying bacteria, which yield free nitrogen, and from the present system of sewage disposal.

According to E. J. Russell (*J. S. C. I.*, 1918, **37**, 45R) one pound of combined nitrogen, properly used in the soil, will yield enough food to supply a man for about five days. Normally, a plant takes up practically the whole of its nitrogen in the form of nitrates, and the most efficient fertilisers are the nitrates of potassium, calcium, and sodium. Other nitrogen compounds must first be oxidised to nitrates in the soil. Ammonia is rapidly oxidised to nitrates by soil bacteria, and ammonium salts applied to the soil are converted into nitrates before the plant is ready for all the nitrogen supplied. Protein nitrogen, amino-acid nitrogen, and amide nitrogen, such as are present in farmyard manure, are also rapidly oxidised by soil bacteria. Calcium cyanamide is first converted into ammonia and then into nitrate in the soil. Other nitrogen compounds, such as diazo-compounds, nitro-compounds, and ring-compounds, are, as far as is known, useless as fertilisers. The relative values of combined nitrogen in the various forms have been stated as follows: Nitrate nitrogen, 100; Ammonia nitrogen, 95; Cyanamide nitrogen, 85 to 90, or more; Protein nitrogen, 70 to 80.

The natural sources of combined nitrogen are twofold: First, electrical discharges in the atmosphere, causing union of nitrogen and oxygen, with the ultimate production of nitrates and nitrites.* By this means it is estimated that every acre of ground in Great Britain is enriched annually to the extent of 11 pounds of combined nitrogen. In the tropics, where thunderstorms are more frequent, the amount is larger.

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* See, however, Moore, *J.C.S.*, 1921, p. 1555.

Second, certain leguminous plants, such as peas, beans, vetch, and clover, possess root nodules containing bacteria which are capable of fixing atmospheric nitrogen in their growth, and so enriching the soil in combined nitrogen (Hellriegel, 1866). Attempts to use cultures of these bacteria in promoting the nitrification of the soils—*e.g.*, in the forms of "Nitragin" or of "Bacterised Peat"—have not, however, proved encouraging.

Numerous experiments have been made with a view to the practical utilisation of the bacterial oxidation of ammonia to nitrates, notably by Muntz and Lainé, of the Pasteur Institute, and by Lunden and Thorssell of Stockholm. The former used a mixture of charcoal, turf, and chalk, inoculated with nitrifying bacteria, through which a dilute solution of ammonium sulphate was percolated. The optimum temperature was found to be 30° C. The bacteria cannot tolerate too concentrated solutions of ammonium salts, but are unaffected by considerable amounts of nitrates. The liquor is therefore passed from one nitrifying bed to another, and enriched by the addition of a portion of ammonium sulphate between each bed and the next. A solution of calcium nitrate is obtained, which may be precipitated with ammonium carbonate to form ammonium nitrate. The highest concentration of calcium nitrate attained was 62·25 g.-lit.; the nitrification then ceased. In semi-technical experiments the supply liquid contained 5·7 grammes nitrogen as calcium nitrate, and 1·3 grammes nitrogen as ammonia, per litre.

Lunden and Thorssell (*E. P.* 15,667, 15,668, 15,670, and 15,671 of 1918) use a nutrient solution containing a requisite amount of the oxidation product, as well as ammonium salts for oxidation, and the ammonia to be oxidised may be added in the form of ammonium nitrate. Thus, 1 cubic metre of solution containing 150 kilogrammes calcium nitrate and 8 kilogrammes ammonium sulphate is exposed to the action of the bacteria. After oxidation, the solution contains 160 kilogrammes calcium nitrate per cubic metre. Sixty litres of this solution are now used for the preparation of ammonium nitrate by adding ammonia and carbon dioxide, the calcium carbonate precipitated being put back into the main solution to provide base for the neutralisation of the nitric acid formed.

To the remaining 940 litres are added 60 litres of water, 8 kilogrammes ammonium sulphate, and a suitable amount of calcium carbonate, and the whole sent back to the bacteria beds for further oxidation. Alternatively, 1 cubic metre of solution containing 150 kilogrammes calcium nitrate and 10 kilogrammes ammonium nitrate is used. After oxidation the solution contains 170 kilogrammes calcium nitrate, and 120 litres are set aside for conversion into ammonium nitrate. The solution of the latter obtained contains 166 grammes ammonium nitrate per litre. Sixty litres of this solution, 60 litres of water, and 880 litres of original solution, form the fresh liquid exposed to the action of the bacteria, whilst 60 litres are used for the production of ammonium nitrate. Calcium carbonate is used as substrate instead of turf, and a current of air passed through. The method of cultivating the bacteria is described in *E. P.* 15,669 of 1918; the bacteria may be cultivated in a liquid containing 1 to 2 per cent. of oxygen, and weak bases such as chalk, easily decomposed silicates, soda, etc. The bacteria are obtained from fertile soil. Pure cultures are not essential, but extraneous organisms such as moulds and protozoa are injurious. These may be eliminated by avoiding organic matter in the culture media and adding small amounts of poisons such as phenol, cuprous cyanide, sodium fluoride, and aniline, to which the nitrifying bacteria are very resistant. Toilet sponge is said to form a good substrate.

The objections to such processes are their slowness, the space required for handling the enormous bulks of dilute solutions obtained, and the large amount of fuel required for the evaporation of the latter. Ammonia is much more easily oxidised to nitric acid by catalytic methods (see below).

Sodium Nitrate in Agriculture.

It is known from the work of Stutzen and Hartleb that most plants obtain their protein nitrogen from the soil in the form of nitrates. These nitrates may either be administered artificially to the soil as fertilisers, or may be formed from naturally occurring nitrogenous material by the action of nitrifying bacteria.

There is a continuous movement of these supplies of nitrate, which are carried down by heavy rainfall, only to rise to the surface again as the soil dries. Any form of putrefaction causes a reduction of the nitrates to lower oxides of nitrogen, and finally to ammonia, and the destructive ferment present on straw and other vegetable refuse may even set the nitrogen free in the elementary form. It would therefore appear that the nitrate supply of the soil may be considerably reduced under certain circumstances if the surface is strewn with vegetable refuse.

An ample supply of nitrate is indicated by a luxuriant growth of vegetation, accompanied by a dark green colour; deficiency, however, causes stunted growth, with a yellowish-green colour.

The presence of nitrates has been demonstrated in nearly all families of plants, more especially in the newly formed absorbing roots. Some plants store the supplies of nitrate in their roots during the winter, while in others it is only present in springtime.

Wheat will store as much as 1 per cent. of nitrates in the roots during winter, preparatory for use when growth starts in the spring. These supplies are not washed out by cold water. They may be detected in lessening quantity up the stem, vanishing in the leaves of the growing plant.

In order to get the best results from the use of sodium nitrate as a manure, it should be used in conjunction with phosphatic and potassic manures, more especially when applied to soils deficient in the last-named ingredients.

In consequence of the detailed and special investigations which have been carried out with a view to determining the optimum conditions for the application of sodium nitrate to the soil, there has been a rapid increase in recent years in its use as a fertiliser, the nitrogen content of the salt being very quick in action and wholly available for direct absorption by the plant. The nitrate is very soluble, and its solution permeates quickly through the soil particles. On the heavier soils it is not likely to be washed out by any ordinary rains, while in the case of the lighter soils it should be applied in several small doses after heavy rains, which may have carried away some of the existing soil nitrogen.

Sodium nitrate is especially useful as a nitrogenous manure on soils which are deficient in lime. Acid fertilisers, such as ammonium sulphate, cause a rapid depletion of the lime content of the soil; sodium nitrate, on the other hand, tends to preserve this. Further, there is evidence in support of the view that the basic radical of the salt exerts considerable influence in rendering otherwise insoluble potash available to the plant.

In consequence of this, the addition of sodium nitrate to loamy and heavy soils may make the use of potash manures superfluous, although this is doubtful. Sodium nitrate exerts its influence to the best advantage during the growing stages of most plants; hence it is to be recommended in most cases as a top dressing. Moreover, the ravages of insect pests which often attack crops during the early stages of growth can often be checked by manuring with this fertiliser.

Attributes of Sodium Nitrate as a Fertiliser.

1. It produces improvement in the yield of mangolds, hay crops, grass, vegetables, fodder crops, sugar-cane, hops, citrus, fruit-trees, flowers, etc.
2. Used by itself on a soil well supplied with mineral plant foods, it is efficient when applied as a top dressing.
3. It can be used in admixture with other manures, such as bone-dust, basic superphosphate, phosphatic guano, blood and potash manures (any two or more), together with some ordinary phosphate. The mixture will not deteriorate if stored in a dry place. When mixed with superphosphate it should be used a few days after mixing.
4. Sodium nitrate can be used at any time during the year to stimulate growth, but the most favourable time for its application is in early spring. It should be broadcasted when the plant foliage is dry, to prevent it sticking to leaves, and frequently gives better results when used in several small top dressings rather than in one large dose.

It should not be used in unnecessary excess; $\frac{1}{2}$ or $\frac{3}{4}$ cwt. per acre in the early stages of growth promotes an abundant yield in leguminous plants (peas, beans, clover, etc.). In the case of fruit-trees, citrous fruits will require the application of about 1 pound per tree at a time, and in all from 2 to 6 pounds per annum. Deciduous trees should receive 1 pound per tree a short time before flowering, and a second dose of 1 pound when fruit has set; the amounts may be increased in the case of old or large trees. Small fruits should get from 1½ to 2½ cwt. per acre at similar periods during their growth. The material is best applied during the dry intervals of showery weather, and need not be harrowed into the soil unless the surface of the latter is hard. Exposure on the surface to excessive hot sun is to be avoided.